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THE
Corrosion and Preservation
OF
IRON AND STEEL

BY

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TO THE MEMORY

OF

CHARLES B. DUDLEY

WHO, DURING A LIFE OF SPLENDID SERVICE, WAS ALWAYS READY
TO ENCOURAGE INVESTIGATION, AND WHO EARNESTLY
BELIEVED THAT THERE WAS SOMETHING NEW TO BE
LEARNED IN EVERY BRANCH OF KNOWLEDGE,
THIS VOLUME IS DEDICATED, WITH
PROFOUND RESPECT, BY
THE AUTHORS

PREFACE

It has been found a difficult matter to bring a work of this kind up to date. New material, which touches directly, or indirectly, on the corrosion and preservation of iron and steel, is appearing almost daily in the technical press of the world. The authors have made the effort to include or mention the results of all recent investigations and original researches touching on the subject which have appeared up to the time of going to press, even if to some extent the systematic arrangement of the work has had to suffer by frequent insertions. Although a considerable space is given to the description and results of the researches of one of the authors working in a Government laboratory, no material is included from this source that has not already been printed in official bulletins for free distribution to all persons desiring it. While the book is written mainly to elucidate the electrolytic theory of corrosion (which some one has humorously referred to as "The New Thought" in the protection problem), it is nevertheless hoped that it will be found useful and suggestive even to those to whom the theory does not especially appeal.

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INTRODUCTION

THE OBJECT OF THE WORK

IN the preparation of this work it has been the aim of the authors to present as simply as possible the results of the more recent researches on the corrosion and preservation of iron and steel. The results of these researches have led to the electrolytic theory of corrosion, which it is safe to say is now provisionally accepted by almost all of the authorities on the subject. Friend,¹ who has appeared in several papers in opposition to the electrolytic theory, now very recently states that he is not an adherent of the carbonic acid theory, but rather of the general "acid theory" of corrosion. He agrees, however, that the acid theory is in harmony with the electrolytic theory of ionization. The question at issue, therefore, involves a distinction and not a difference.

The electrolytic action which can be demonstrated taking place when iron rusts in contact with water should not be confused with the rapid destruction of steel in the neighborhood of escaped currents from high potential circuits used for electric lighting or power lines. As a matter of fact, the phenomena do not differ except that in one case there is an external source of energy at work, whereas in the other the energy of electro-chemical action is due to the slow combustion or oxidation of iron. In order to avoid confusion of terms and ideas, it has been proposed that we should speak of the underlying electro-chemical cause of corrosion as autogenous electrolysis, while another suggestion is that the shorter term, autoelectrolysis, should be adopted. There is no reason why these terms should not come into general use, but the fact remains that they have not yet done so; the authors have therefore held to the electrolytic explanation of corrosion, without the introduction of these or other new terms.

¹ See *Electro-Chem. and Met. Industry* VII., 11, 489, Nov., 1909. Also *Jour. Iron and Steel Inst.* 77, 5, 1908.

In the authors' opinion corrosion must be considered an electro-chemical phenomenon, and therefore a special effort has been made to treat the subject in such a manner as to render it intelligible to technologists, even if they are not thoroughly grounded in the underlying principles of physical chemistry.

In the chapter on the theory of solutions an explanation is given of the fundamental electro-chemical principles, without an understanding of which no discussion of the corrosion problem from this point of view is possible. It is hoped that this exposition of the subject will be found helpful by manufacturers, engineers, metallurgists, and, in short, by all persons to whom the rapid rusting and decay of iron is a matter of anxious solicitude. Wherever citations from other authors have seemed to strengthen the development of the subject both as to theory and as to fact, these have been freely made with the fullest credit to the authority quoted. It has been remarked that the omission by some of the prominent workers in this field, to mention in their publications the contributions of others, has been the cause of confusion in the minds of investigators who have had occasion to review and discuss the problem. A considerable body of material has been included which has been already previously published by the authors from time to time in bulletins and papers before technical societies. The object of the insertion of this matter here is to better support the general argument and to preserve it in a more permanent and concrete form. So much has been claimed in regard to the relative rust resistance of iron and steel that it has seemed best to include names of both types of metal in the general title of the book. There are, however, many places in a general discussion in which the word "iron" can be used in its general sense, and whenever it has been possible without leading to confusion this has been done.

The purely metallurgical problem of the manufacture of highly rust-resistant metal has been touched on lightly, as the subject is one on which much difference of opinion exists and little consistent information is available. It is hoped that neither the defenders of Bessemer and open-hearth steels, nor those who believe in puddled and charcoal irons, will find any biased opinions set forth in the succeeding pages.

The tendency to rust is a characteristic inherent in the element known as iron, and will in all probability never be entirely over-

come. Nevertheless, it is perfectly well known that there is the greatest variability both in the manner and rapidity with which different specimens and types of this metal and its alloys suffer from corrosion. Before substantial advance in the manufacture of resistant types and in the protection of all types can be made, a thorough understanding of the mechanism of corrosion and the function of protective coatings must be obtained.

The demand of the engineer and architect for the most advanced knowledge regarding protective coatings for iron comes as a result of the failure of many types of paint now in use. Technical literature is replete with information regarding the protection of iron, but probably the most remarkable advance in knowledge of this subject has taken place during the last few years, and almost wholly as a result of a well-planned series of investigations recently undertaken by a number of independent workers. The aim of the authors is to present the latest developments on this phase of the subject in a general way so that the underlying principles which govern corrosion can be applied by each investigator to his own particular problem.

So diverse a subject as the corrosion and preservation of iron would become encyclopedic, if the attempt were made to take up every phase in detail, or to abstract the literature of the subject from the technical and scientific journals of the world. The protection of boiler tubes presents a very different problem from the protection of bridge structures, and yet the same main principles can be applied to the consideration of each case. It is this point that the authors have had in mind, and while a number of specific cases of corrosion are presented and discussed the main object has been to treat the subject in a general way. For this reason no separate chapters are included on special phases of the problem, such for instance as the corrosion of boilers, the corrosion of fence wire, or the corrosion of ships' bottoms. All these subjects, as well as many other special cases of corrosion, are, however, brought up and treated as special instances to which the general discussion applies. On this account those readers who propose to use this work as a reference book in special cases of inquiry will depend upon the index to the volume rather than upon chapter headings to guide them.

That much of the work which has been done along different lines in the past in the effort to supply adequate protection for

iron and steel has been unsatisfactory requires no proof. Unfortunately, much of this work has been based on purely empirical knowledge of the subject, that is to say, it has depended on individual experience or observation without due regard to science and theory. Thus, for instance, we find one engineer experimenting with red lead as a prime coating material, and reaching a conclusion favorable to its use, while another engineer as a result of his own observation arrives at a quite contrary opinion. The case comes up for discussion before an engineering or technical society and adherents to the two sides of the argument are not wanting to carry it on to indefinite lengths. The old question in regard to who is to decide when doctors disagree applies quite as well to such a case as this, and less learned people are perplexed by the violent controversies between those who are supposed to be expert. A more scientific acquaintance with the technology of protective coatings from the standpoint of recent investigations would at once suggest that red lead, like other protective agents, is not a standard substance, and that material from different sources might or might not contain stimulative or accelerative impurities or properties. This same empiricism may be noted in numerous other phases of the protection problem, as in the steel versus iron controversy, or in the rival processes for galvanizing and tinning. A theory serves the purpose of a well-articulated skeleton, to which may be attached the sinews and muscles represented by observed facts. If most of the results of experiment and observation find their natural and prepared points of attachment the theory is, to say the least, useful as a working mechanism, even if some observations are found difficult to fit in. As a matter of fact the recent electrochemical theory of corrosion presents few if any difficulties which require to be explained away, while on the other hand, it furnishes a rational explanation for many previously unexplained occurrences and phenomena.

In presenting and developing the electro-chemical explanation of corrosion the authors' hope is to put into the hands of technologists generally a working theory which will be both suggestive and practically useful.

THE CORROSION AND PRESERVATION OF IRON AND STEEL

CHAPTER I

THE PROBLEM OF CORROSION

Importance of the Corrosion Problem. — The importance to the human race of arresting the rapid decay of structural iron has never been denied. It is almost impossible to find a volume of transactions of an engineering or learned technical society for years past that does not include papers and discussions on this all-important subject. The different theories that have been formed to account for the effects produced have been numerous, and the suggested treatment and methods for protection, without end. As Sang in a recent résumé of the whole subject aptly puts it:¹ "The decay of iron and steel by corrosion, if natural agencies are allowed to act on them, is far more rapid than that of wood and other materials of construction. Steel is being used more and more every day for buildings and other permanent structures and therefore on the prevention of this decay depends the permanency of these works and the safety of future generations. Were it not for iron and steel, the erection of large works of engineering would be impossible and their very size and consequent high cost, representing as it does a large sum of human energy — which is after all the only true foundation for wealth — make it a duty to preserve them from decay.

"On a structure like the Forth bridge a number of men are kept at work, cleaning rust-spots and repainting. The wise course of preserving such structures for the use of our descendants is not generally followed, and it is only when accidents like the one at Charing Cross Station in London take place, that interest is revived, for a time, in the question. Wood, in referring to the roof of a gas-works in New York City which collapsed for lack of attention, forecasted a similar fate, sooner or later, for

¹ Proc. Eng. Soc. West. Pa., Vol. XXIV, 10, 493.

structures like the viaducts of the elevated railway of the same city, which almost casual observation will show are repainted over the rust without cleaning.

"On account of this necessity of combating corrosion, it is imperative that engineers arrange the design so that every part of structural works be readily accessible for frequent inspection. It has been truly said that 'wrought iron is not only a bad but a dangerous material if neglected'; this is equally true of steel."

† *Contending Statements as to Rust Resistance of Different Types of Metal.* — No attempt will be made in this work to decide between contending statements as to the relative rust resistance of wrought iron, charcoal iron, and the various types of steel. The authors are satisfied to reiterate their previously published opinion that there is great variation in each type of metal in rust resistance and that in this respect there are good and bad irons just as there are good and bad steels. If this is true, and a mass of evidence seems to support the statement, it is useless for manufacturers of the different types, through their agents, to engage in endless polemical debates over the comparative excellence of their respective products. The proper control of unavoidable impurities, their homogeneous distribution and a careful heat treatment, particularly as far as the annealing processes are concerned, will improve the rust-resistant quality of metal, whether it is called iron or steel, and regardless of the method by which it is made.

It is now very generally admitted as the result of recent researches by a number of investigators that a state of stress or strain in a metal invites rapid corrosion, as will also a burnt condition of the metal leading to high porosity and the presence of occluded gas and blow holes. Sang says in regard to this point:¹ "Carelessness of manufacture, which tends to heterogeneity, is an invitation to corrosion and in itself goes far to explain why modern steel, which is tortured into shape at such a high speed that the molecules are not permitted to readjust themselves, is said to be more corrodible than the metals produced a generation ago; in those days iron and steel were produced in small quantities, without the addition of other metals, and were rolled slowly and allowed to cool naturally. The internal strains due to mechanical treatment are not to be confounded

¹ Proc. Eng. Soc. West. Pa., Vol. XXIV, 10, 511.

with the unevennesses in the distribution of the impurities due to segregation in cooling; these mechanically induced strains are really equivalent to straining the metal beyond the elastic limit which, as will be seen later, makes it more corrodible. Moreover, the tonnage-craze, from which the quality of product in so many industries is to-day suffering, is causing to be placed on the market a great mass of material, only a small proportion of which is *properly* inspected, which is not in proper condition to do its work: — rails and axles which fail in service and steel skeletons for high buildings which may carry in them the germs of destruction and death.” With this summing up the authors are in complete accord and no further space in this work will be given to the discussion of the comparative merits of iron versus steel in the resistance to corrosion.¹

That the old, largely hand-worked metal of about thirty years ago is superior in rust-resisting quality to the usual modern steel and iron is attested by the recorded evidence of a large number of observers. Many citations could be given to prove this and the examination of the discussions of numerous papers before engineering and technical societies seldom fail to bring out evidence of the very general belief in the superiority of the older product. A more detailed discussion of this subject must be postponed to a later chapter. The accompanying illustration (Fig. 1) showing a contrast between two nails is interesting though not unusual. Sample A is a forged nail that was used in the old Masonic Hall in Richmond, Va., and was probably driven in 1807. It was in service about one hundred years and for a large portion of that time was freely exposed to the weather, as the old clapboarding rotted away. The illustration shows that even the thin edges of the forged head are still sharp and uncorroded. Sample B is an ordinary modern nail after six months' exposure in a wooden gutter on a roof at Washington, D. C.

No thoughtful person supposes that it would be practically possible to return to the earlier laborious methods of iron manufacture, in order to produce metal highly resistant to corrosion. The modern problem must be solved by modern economic methods,

¹ For a full discussion of this subject by advocates of various types of metal the reader is referred to the Transactions of The American Society for Testing Materials, for years 1906-7-8, also to Transactions American Institute of Mining Engineers for 1905.

and there is no reason to suppose that great improvement will not be made in the quality of both iron and steel, as soon as the principles governing the rate and kind of corrosion which takes place on different types and kinds of iron are thoroughly established. These principles will be brought out in detail in succeeding chapters.

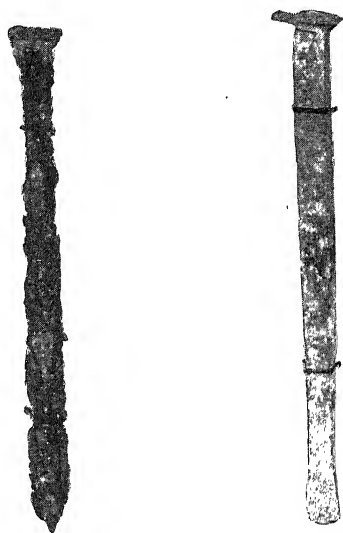


FIG 1. — Showing the relative corrosion of a modern steel nail and an old forged nail.

Corrosion and Conservation. — No discussion of the corrosion problem is complete without reference to its bearing upon the conservation of natural resources. In the introduction to an address before a recent meeting of the Iron and Steel Institute of Great Britain, one of the authors called attention to the importance of this phase of the problem in the following words: "It is significant of the present age that the tendency of thought among all nations is toward conservation of natural resources. Increasing consumption of the world's supplies and constant decay of materials menace the future of the human race. It is evident that carbon, from which we derive energy, and iron, which provides the principal means of applying energy, are the materials which should particularly engage the attention of those

who are studying the problems of conservation. The annual production of pig iron in the United States alone grew from about 14,000,000 tons in 1900 to about 26,000,000 tons in 1907, and while for the year 1908, owing to industrial conditions, it decreased to about 16,000,000 tons, it seems sure to again show an increase in the near future. How much of the enormous and constantly increasing world's production of iron and steel is wasted for lack of adequate preservation? Where will the growth of demand stop, and how many years will the world's ore supply stand the drain upon it? These are questions of vast importance, the answers to which can only be vaguely guessed. One thing seems certain, namely, that civilization must learn to conserve more efficiently its stores of iron and steel already manufactured, and seek methods to prevent the almost resistless tendency of iron to return to its lethargic union with oxygen, from which it was won only by the consumption of vast quantities of the ever dwindling coal supply. It is not generally realized that about four tons of coal or its equivalent is used in preparing one ton of finished steel from the ore. The world's store of gold is not subject to loss by corrosion, but suffers to some extent from attrition, owing to the softness of the metal. If steel could by any means whatsoever be ennobled and thus protected from the inevitable decay due to corrosion, future conditions for all possible years to come could be viewed with complacency. There exists at Delhi, India, an iron monument that, since the dim beginning of history, has been exposed to the weather without rust or decay, and yet this column has been provided with no protective coating, other than that which the atmosphere has itself formed upon it. Could we to-day, with all our boasted knowledge and our great pneumatic processes, build its like? It is probable that we could not, and yet an art is not necessarily lost forever. It is simply a question whether or not it is worth our while to rediscover it."

The President of the Iron and Steel Institute in discussing this paper stated in his remarks that no doubt this was a phase of the subject which was most prominently before the world at the present time, and that nothing could be more valuable to the iron industry at large than that the question of the preservation of the metal which they were engaged in manufacturing should be investigated and solved.

These citations serve to bring out the great importance of the corrosion problem and show the earnest attention that is being given to it by metallurgists and learned bodies.

Three Phases in the Problem of Preservation.—One of the writers has in previous papers¹ referred to the fact that the problem of the preservation of iron has three distinct phases. The first phase has to do with the manufacture of a metal highly resistant to corrosion, such as is represented by the iron column of Delhi, Fig. 2, or the splendid examples of hand-forged metal that have come down to us from past centuries, and with which we may contrast the pitted, lacelike condition of specimens of modern steel after only a few years' exposure to the atmosphere. The illustration, Fig. 3, shows the condition of certain members taken from a signal bridge on an American railroad.² The structures were about twelve years old and exhibited great differences in the rate of corrosion of different members. This point will be discussed more fully later on, but the photographic reproduction serves to illustrate very forcibly the lacelike condition assumed by metal undergoing rapid corrosion.

The second phase of the subject concerns the general subject of protective coatings, which may consist of other metals, such as zinc, tin, copper, and lead, or of oil paints, varnishes, lacquers, and bituminous materials, or, finally, the production of a higher oxide on the surface, as in the Bower-Barf, Wells, and Speller processes. The third phase includes the interesting study of the passive condition which iron is capable of assuming, and the possibility of maintaining the surface in such an ennobled condition, either by the use of inhibitive pigments in paint compounds, or by the use of electric currents as described later on.

Discussion Aroused by the Electrolytic Theory of Corrosion.—Many discussions³ have arisen in regard to the several rival

¹ U. S. Dept. Agr., Office of Public Roads, Bul. 30, 1907; Trans. Am. Soc. for Testing Materials, 1907, 7, 209; Trans. Am. Electro-Chem. Soc., 1907, 12, 403.

² Samples and information furnished by Mr. J. P. Snow, Bridge Engineer, Boston and Maine R. R.

³ Am. Soc. Mech. Eng., Trans. 1894, 15, 998; *ibid.*, 1895, 16, 350, 663; Zts. Elektrochemie, 1903, 9, 442; Treadwell and Hall, Analytical Chem., 1907, p. 92; Manchester Lit. Phil. Mem., 1871, 5, 104; Jour. Iron and Steel Inst., 1888, 129–131; Proc. Chem. Soc. (Lond.), 1906, 22, 101; Jour. Chem. Soc. (Lond.), 1905, 87, pt. 2, 1548; Jour. Am. Chem. Soc., 1903, 25, 394; The Analyst, 1905, 30, 232; Trans. Chem. Soc. (Lond.), 1906, 98, 1356.

theories of corrosion, but the evidence which has been collected in numerous recent researches appears to the authors to prove

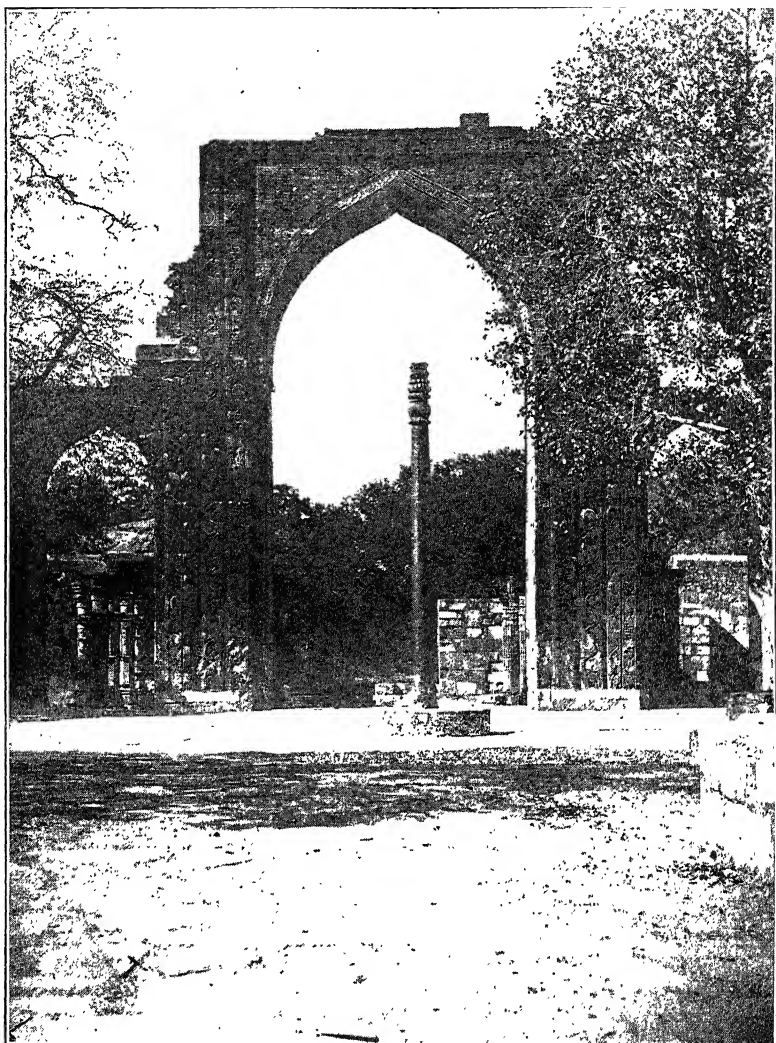


FIG. 2. — The Iron Column of Kutab Minar Delhi, India, erected 900 B.C.

beyond argument that the corrosion of iron, like that of other metals, is an electro-chemical phenomenon. Some confusion has arisen in regard to this contention which the authors take

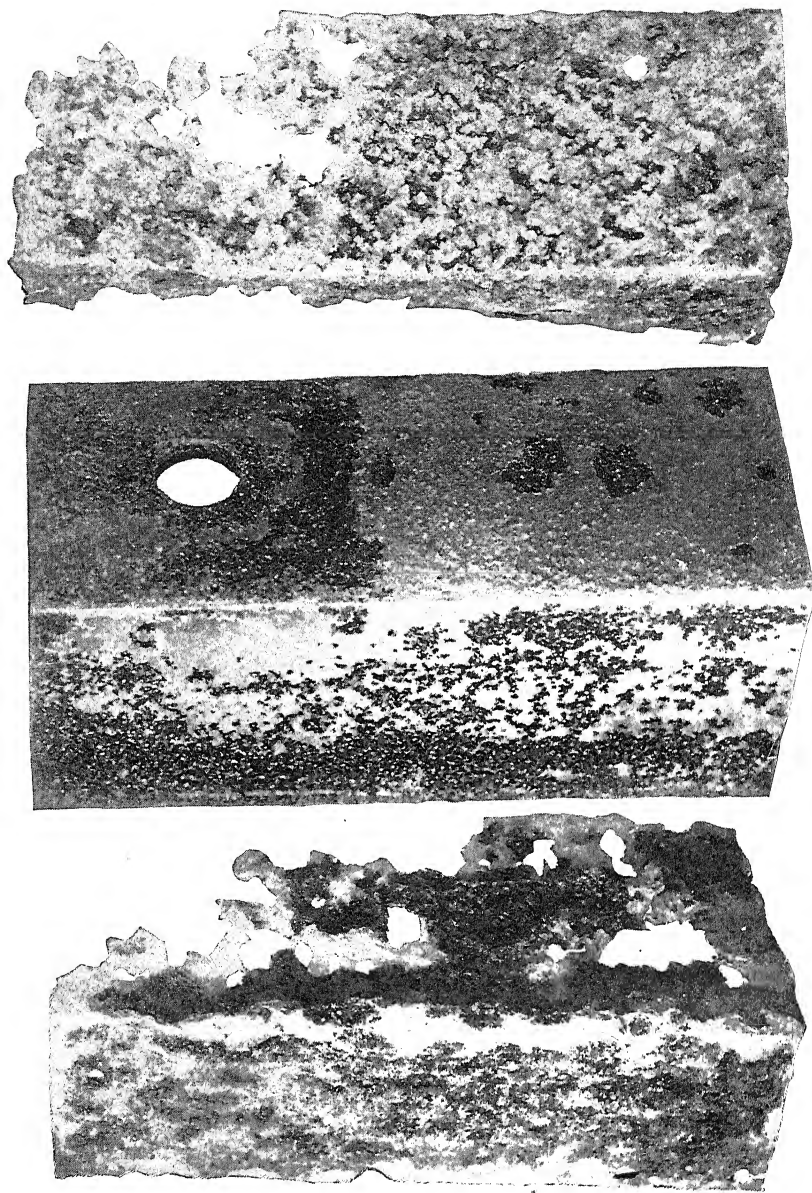


FIG. 3 — Showing unequal corrosion of different members of the same structure. The lacelike condition of badly corroded steel is also shown.

this occasion to explain. H. M. Howe, an eminent authority, has stated:¹ "Electrolytic action surely hastens corrosion very greatly, and in practice it may well be true that nearly the whole of corrosion is electrolytic. But imagine the case of absolutely pure iron, without stress or slip planes, immersed in pure water containing dissolved oxygen. Will not the iron go into solution till the solution tension is reached, and will not the iron so dissolved oxidize, precipitate, and leave room for more iron to dissolve? It seems to me in this and like ways corrosion may go on without electrolysis. If so, then electrolysis is an aggravator and hastener of corrosion, but not essential to it."

Every one interested in the subject who will read the succeeding chapter on the Theory of Solutions will understand that iron which is pushed into solution by its solution tension immediately ionizes and assumes an electric charge and that probably iron is never in such a quiescent condition that some polarization does not take place. The further discussion of this point as well as the consideration of the effect of outside or extraneous currents of electricity in effecting corrosion must be postponed to a later chapter.

Influence of Various other Elements Contained in Manufactured Iron. — In considering the corrosion of iron it is important to remember that iron is a metal which readily combines with or dissolves nearly all the other elements. With possibly one or two exceptions, there are no elements that do not either dissolve in or combine readily with iron. It is also unique in the fact that very small quantities of impurities suffice to entirely change its physical characteristics. On account of this fact metallurgists scrutinize the hundredth of a per cent. of some of the principal impurities that are generally associated with this metal. This is particularly true, for instance, of the element phosphorus. It is so important to modern metallurgy that the amount of phosphorus should be controlled in certain forms of steel that an animated discussion is going on at the present time between certain interests as to the control of the amount of phosphorus that steel shall carry, and the question at issue amounts to no more than a few hundredths of one per cent.

Manganese is also an element which is nearly always associated in modern metallurgy with iron and steel. Manganese

¹ Trans. Am. Soc. for Testing Materials, VIII, 278, 1908.

decreases the electrical conductivity of iron, and as the percentage of manganese, starting from zero, rises, the electrical resistance increases up to a certain specific maximum. It will be seen that if the presence of manganese in iron raises the electrical resistance, any variation in the distribution of the manganese means that there will not be a constant electrical conductivity throughout its mass, or on any given surface. There is abundant evidence to show that manganese associates itself to a considerable extent with sulphur when both these impurities are present in steel.¹ That manganese sulphide shows a difference of electrical potential against iron is also well known. One who is familiar with the methods of modern metallurgy knows that the manganese is added for certain specific purposes, not as a rule quantitatively, but in accordance with the views of the iron master who has control of the mill or furnace. Moreover, the manganese is usually added by throwing lumps of ferromanganese into the molten metal, either in the furnace itself or in the ladle into which it has been poured. Chemists know the extreme care that has to be taken in order to get uniform mixtures of substances in the course of chemical operations. On the large scale on which metallurgical processes are conducted, even if it were possible to take great care in the mixing, it still happens that when iron is cooled from the molten state segregation takes place — that is to say, the impurities, although they may have been thoroughly mixed in the molten mass, do not remain homogeneously distributed after the metal is cooled.

For these reasons we must remember that in studying iron and steel from the standpoint of their stability, under the conditions of service, we are not dealing with homogeneous pure metal.

Problems Confronting Manufacturers of Structural Materials.— If we consider the results of recent experimentation along the lines of the three phases as indicated above, we find that considerable progress has been made in the course of the last few years. Many leading manufacturers of iron and steel have been paying special attention to the careful control of impurities, and the heat treatment of their products, as well as to the equally important problem of evolving rust-resistant metallic coatings in the various processes of galvanizing with zinc and special

¹ Fay, Proc. Am. Soc. Test. Mat., VIII, 74 (1908).

alloys.¹ The condition of maintained passivity which has come to be known as "inhibition" is especially a problem for the paint manufacturer and will be dealt with in detail in later chapters of this book.

One phase of the corrosion problem which is of the utmost importance and which has been discussed with anxious foreboding is the possible corrosion of steel embedded in concrete. The consensus of opinion among engineers and investigators of the corrosion problem appears to be that concrete furnishes ample protection to steel embedded in it, except in certain cases in which infiltrating or percolating waters find a way through the concrete, washing away the free alkali present in the form of lime or calcium hydroxide. The reasonableness of this explanation will appear later on.

Local Conditions Affecting Corrosion. — It is quite apparent that the corrosion problem has increased steadily with the growth of civilization, for the waste gases of combustion pollute the atmosphere and the water with which iron may come in contact, and besides this there are many stray electric currents escaped from high potential circuits which undoubtedly aid in the work of destruction. H. M. Howe, in making a plea for modern steel, has said:² "The fact that steel has come into wide use simultaneously with a great increase in the sulphurous acid in our city air and of strong electric currents in our city ground may well lead the practical man, be he hasty or cautious, into inferring that the rapid corrosion of to-day is certainly due to the new material of to-day, steel, whereas, in fact, it may be wholly due to the new conditions of to-day, sulphurous acid and electrolysis."

While the above statements are perfectly true they do not furnish a complete and satisfactory explanation of the whole problem. Take the interesting case of the steel light-ship, U. S. Light-Vessel No. 71, built in 1897, which was anchored at Diamond Shoal off Cape Hatteras for eleven years, and was towed in at the expiration of that time so that 8400 four-inch bolts

¹ Since the writing of this paragraph, patents have been granted for a process of producing exceptionally pure iron in basic open-hearth furnaces which is claimed to be slagless, degasified and easily workable. Since the effort to produce this type of metal was originally suggested by one of the authors it is proper to record here its successful accomplishment on a commercial scale.

² Proc. Am. Soc. Testing Materials, 1906, VII, 155.

which were destroyed by accelerated electrolytic action could be replaced.¹ In such a case as this serious damage occurred after eleven years, due to electrolytic corrosion, although the material was subjected to no stray currents or sulphurous acid gases. Probably not all the bolts were in actual contact with salt water, although the general saltiness of the atmosphere undoubtedly stimulated the action. The condition of the destroyed bolts is well shown in the illustration, Fig. 4. The discussion of this and similar cases of corrosion will be postponed to a later chapter.

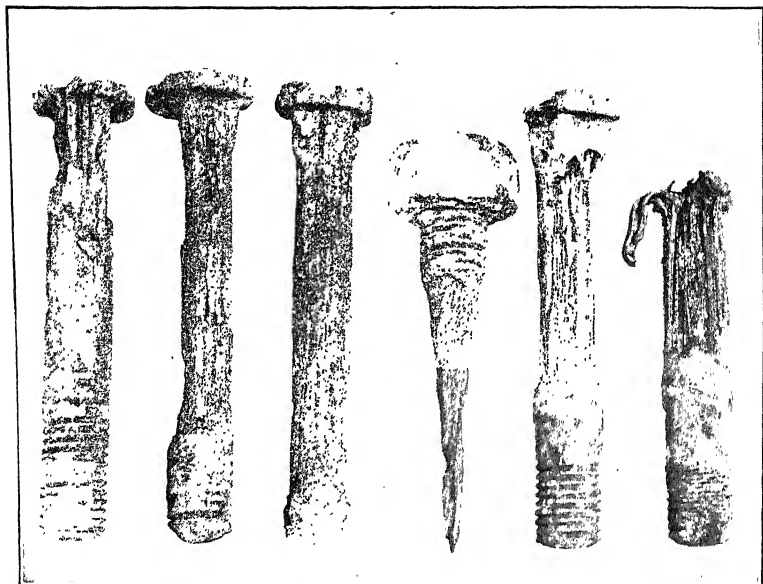


FIG. 4. — Showing the corroded condition of bolts taken from the U. S. Light-Vessel, No. 71.

The Working Knowledge Necessary to the Understanding of the Corrosion Problem.—It is not possible to make an intelligent study of the problem of corrosion without at least a working acquaintance with the principles of the new knowledge in physics and chemistry which has gone so far to elucidate and explain many heretofore obscure phenomena. It is, however, the opinion

¹Information and specimens furnished by A. B. Johnson, Supt. Light-house Establishment, 5th District, Dept. Commerce and Labor, also by Robt. L. Russell, Commander, U. S. N.

of the authors that the groundwork for a proper understanding can be acquired by any person with some technical knowledge and experience, even if chemistry, and more particularly physical chemistry, has never before engaged his attention. To this end the following chapter on the theory of solutions has been included. In the treatment of this chapter the effort has been made to present in the simplest possible way the underlying principles which enter into the corrosion problems in their most recent and modern aspects. The new theories which attempt to explain corrosion have hitherto been presented mainly before learned technical bodies, and in the columns of the highly scientific and technical press. It is the earnest hope of the authors that a careful perusal and study of the following chapter will enable any intelligent person who may be interested in the problem to understand the discussions and data presented in the succeeding chapters.

CHAPTER II

THE THEORY OF SOLUTIONS

Water a Universal Solvent. — Water is the universal solvent, and it is doubtful if there is a form of matter in existence which is not to some extent dissolved, disintegrated, or otherwise changed by it in the course of time. The action of water is not, however, to be considered as universally destructive, for it is the medium by means of which, and in which, synthesis as well as decomposition takes place in nature. Whether the action of water is to be considered as destructive or constructive depends therefore on the point of view. For instance, the immense bodies of iron ore on which we must always depend for our supplies of iron were undoubtedly originally formed under the action of water, and now once more water carries on the attack on our finished iron and steel, which has been laboriously smelted and reduced from the ore at the expense of vast quantities of free carbon. To the layman iron is an insoluble substance as far as water alone is concerned, but as has been pointed out, when we speak of a substance as being insoluble, we may be merely employing a relative term. If the water is impure, that is to say, if it already contains slight amounts of dissolved substances, its action on any given body is modified. Whether the solvent action is stimulated or inhibited depends upon the nature of the case.

Solution Pressure. — Leaving aside substances usually classed as insoluble, we will for the present consider only those which have a decided and appreciable solubility in pure water. Such a body, when immersed or brought into contact with water, tends to pass into solution; that is to say, its molecules or atoms (depending upon whether the substance in question is a compound or a simple element) tend to distribute themselves equi-spatially among the molecules of the solvent. The driving force which produces this tendency, and which is known as solution tension or solution pressure, is exactly analogous to the pressure exerted by a gas or vapor confined in a vessel, as for instance, in the

case of steam in a boiler. But just as the rising steam pressure in the boiler will tend to resist the evaporation of the remainder of the water, the growing number of free particles entering the solution will produce a back pressure which tends to resist the entrance of more. This back pressure acting against solution tension is called osmotic pressure, and the class of phenomena which it produces is known as osmosis. It is at once apparent that for any given substance at a given temperature, its maximum solubility would be reached just as soon as the solution pressure and the osmotic pressure were equal. It is also apparent that any outside cause operating on the system, which tended constantly to lower the osmotic pressure, would allow more and more of the substance to enter into solution so that the action would become continuous, provided the supply of solvent and solute was maintained. This point is an important one in this discussion, inasmuch as it has a direct bearing on the corrosion of iron.

Osmotic Pressure. — The existence of osmotic pressure was first recognized by the Abbé Nollet about the middle of the eighteenth century. He used animal membranes for demonstrating the pressure. A glass tube closed at one end with animal parchment was filled with alcohol and plunged into a vessel of water. The alcohol tended to dissolve or diffuse into the water and the water into the alcohol, but alcohol cannot pass rapidly through a parchment diaphragm, whereas water can. The consequence was that the level of liquid rose in the tube, revealing the existence of osmotic pressure. Diaphragms which allow the passage of water molecules but resist the passage of substances soluble in water are known as semi-permeable membranes. Traube in 1867 discovered that by depositing a film of a gelatinous preparation of copper ferrocyanide in a suitable manner very good artificial semi-permeable membranes could be formed. This method of measurement has been improved and developed by Pfeffer in Germany and later by Morse in the United States. The copper ferrocyanide is now by an ingenious process deposited as a film inside the walls of a clay cylinder to the top of which the manometer tube for measuring the pressure is luted. It is only necessary here to bring out the fact that osmotic pressures and therefore solution pressures represent values of very considerable magnitude. This is best shown by results obtained by Pfeffer

working with dilute solutions of cane sugar. Here again the water passes through the semi-permeable film while the sugar molecules are stopped so that the pressure can be recorded in the manometer tube in barometric readings.

Pfeffer's results, which were taken at about 14° Centigrade, are as follows:

C = Concentration of Solution in Per Cent.	P = Osmotic Pressure in Centimeters of mercury	P' = Osmotic Pressure in Inches of mercury	P'' = Osmotic Pressure in Atmospheres
1 per cent.	53.5	21.0	0.70
2 per cent.	101.6	40.0	1.33
4 per cent.	208.2	82.0	2.73
6 per cent.	307.5	121.0	4.03

It will be seen from this that the osmotic pressure exerted by a six per cent. solution of sugar is equal to about four atmospheres, or reduced to ordinary terms sixty pounds to the square inch. Sugar, of course, is a very soluble substance and its solution pressure is high, but that even the more insoluble substances have solution pressures of definite and appreciable magnitude is incontestable.

If a strip or rod of polished steel is plunged into a clear glass cylinder containing distilled water and placed so that it can be observed in a strong light, it will be seen that in the course of a few minutes delicate festoons of a whitish brown substance are clouding the sharp edge or outline of the steel specimen and falling away from the surface. This phenomenon furnishes evidence to the eye that the iron has a direct solution pressure, for the whitish brown substance which is forming is a hydrated oxide or so-called hydroxide of iron, and cannot be formed unless iron first passes into solution. Careful observation of this simple experiment will bring out another point which has an important bearing on our subject. It will be noted that the festoons of hydroxide do not appear at all points of the polished surface, but seem to segregate at certain points or areas, leaving others still bright and unattacked. This observation furnishes the first indication that the solution tension of iron is not the same at all points on the surface. This fact is important to the consideration of the corrosion of iron, and will be taken up again after the principles governing solutions in general have been presented.

It has been found possible to illustrate the uneven solution tension of steel rods immersed in water and very dilute electrolytes. A photographic representation of the appearance of three polished steel rods after a few hours' immersion is shown in Fig. 5.

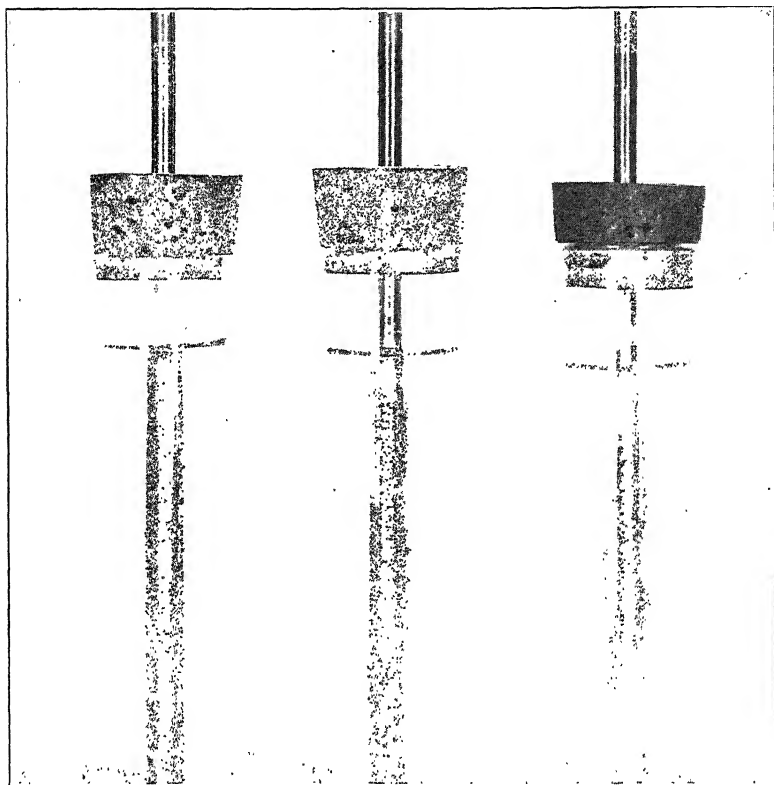


FIG. 5. — Showing the unequal solution tension and rusting of three steel rods immersed in fresh water, sea water, and dilute sodium nitrate.

Relations between Osmotic Pressure and Gas Pressure. — Pfeffer's object in carrying out his researches was to study the role played by osmosis in certain physiological processes, such for instance as the swelling and bursting of seeds, and the movement of sap in plants. It was reserved for Van't Hoff to make the wonderful observations and deductions which, published in an epoch-making paper in 1887¹ was destined to become the foun-

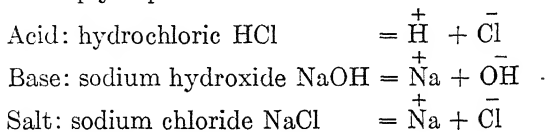
¹Zeit. Phys. Chem., 1, 481.

dation of a new chemistry. The law of Boyle for gases points out that the pressure of a gas varies directly with its concentration, and the general gas law is simply expressed by the formula, $PV = RT$, where P is the pressure, V the volume, T the temperature, reckoned from the absolute zero (-273° Centigrade), and R a constant. Using Pfeffer's results, Van't Hoff pointed out that *the osmotic pressure of a solution of cane sugar is exactly equal to the gas pressure of a gas having the same number of molecules in a given volume*, when the temperature is the same in both cases. This is a surprising generalization, and especially so when we consider the different conditions under which gas molecules and the molecules of a dissolved substance are acting. Nevertheless, still greater surprises were in store, for Van't Hoff further pointed out that while one class of substances which were chiefly organic in their nature conformed with the gas law, another class in which could be included the acids, bases, and salts of inorganic chemistry gave osmotic pressures in dilute solutions, in many instances about twice as high as they ought to if they were in conformation with the generalization. It was at this point that Arrhenius, a Swedish physicist, in 1881 made his great contribution to the dawning science of physical chemistry. Arrhenius developed the discussion of Van't Hoff's deductions as follows¹: If a gas shows a deviation from the gas law, as many of them do at high temperatures, we explain this by supposing that the molecules of the gas which are composed of two associated atoms (as, for instance, hydrochloric acid, which would be expressed molecularly by the symbol $H - Cl$), break down at certain critical temperatures into simple atoms, thus providing twice as many free particles in a unit space. Arrhenius then proposed to apply the theory of dissociation to the molecules of inorganic substances in solution and inquire whether they were not split up on entering solution into constituent particles, or, as he called them, *ions*.

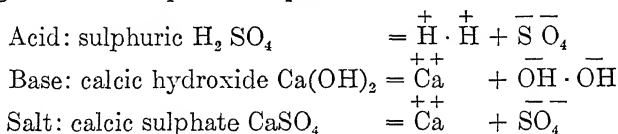
The Theory of Electrolytic Dissociation. — The theory of electrolytic dissociation, as it is stated at the present time, holds that when acids, bases, and salts are dissolved in water to form dilute solution, they break down or dissociate into ions. Ions are atoms or groups of atoms carrying in relation to their masses enormous charges of static electricity. The reason why these charges are not apparent in the molecule is because they are of

¹ Zeit. Phys. Chem., 1, 631.

necessity always equal and of opposite sign. These dissociation reactions are simply expressed as follows:



or to give more complex examples:



The positive hydrogen ion is the distinctive characteristic of all acids in solution, just as the negative hydroxyl ion (OH^-) is the characteristic of all bases in solution. Hydrogen, in spite of the fact that it occurs and is generally known as a gas, belongs to the type of elements which are called metals.

This subject can be more clearly set forth by quoting from a recent excellent text-book on physical chemistry:¹

"Each compound dissociates into a positively charged part called a *cat-ion*, and a negatively charged part, an *an-ion*. These ions may be charged atoms as the above cations, or groups of atoms as the anion OH^- . The cations are usually simple atoms charged with positive electricity. The cation of all acids is hydrogen; the nature of the anion varies with the nature of the acid. It may be chlorine, bromine, the NO_3 group, SO_4 , etc. The anion of bases is the group OH^- ; the cation varies with the nature of the base. It may be potassium, barium, ammonium, etc. The anions and cations of salts both vary with the nature of the salt. They depend upon the nature of the acid and the base which have combined to form the salt.

"It was stated that hydrogen is the cation into which all acids dissociate. It may be added that this is the characteristic ion of all acids, and whenever it is present we have acid properties. Further, we never have acid properties unless there are hydrogen ions present. The same may be said of the hydroxyl ions into which bases dissociate. This is the characteristic ion of bases.

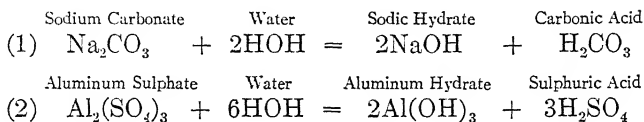
¹ Jones, Elements of Physical Chemistry, MacMillan (1909), pp. 211-212.

"It has been repeatedly urged that the theory claims that a compound like potassium chloride dissociates into potassium and chlorine, and since neither potassium nor chlorine can remain in the presence of water under ordinary conditions without acting upon it, the theory is self-evidently wrong. This objection, like so many others, is based upon an imperfect understanding of the theory. No one has ever claimed that a compound like potassium chloride dissociates in the presence of water yielding atomic or molecular potassium, having the properties of ordinary potassium. The products of dissociation are a potassium ion and a chlorine ion, and the potassium ion is a potassium atom charged with a unit of positive electricity. There is no reason whatever for supposing any close agreement between the general properties of a potassium atom and those of a potassium atom charged with electricity. About the only property which we would expect to remain unchanged is that of mass, and the mass of an atom is not changed by charging it. The properties of atoms are doubtless very closely connected with the energy relations which obtain in or upon the atom. When we change these fundamentally, as by adding an electrical charge, we would expect fundamental changes in properties; and such are the facts. It can be safely stated that whatever may be the ultimate fate of the theory of electrolytic dissociation, it will never suffer seriously from any such objection as that just referred to."

Hydrolysis. — We have now familiarized ourselves with the principles of electrolytic dissociation in which certain substances in solution are broken down into constituent ions. We shall now have to consider a different form of dissociation in which ions and electrical charges are only indirectly concerned, but which has a bearing on many of the problems of the corrosion and preservation of iron. It has long been known that compounds which are formed by association of a weak acid with a strong base-forming element have an alkaline reaction in solution, while conversely a compound made up of a strong acid with a weak base will tend to show an acid reaction. Thus, nearly all carbonates of strong bases, such as potassium, sodium, calcium, and barium, are alkaline, whereas nearly all the salts of very weak bases, such as aluminum, are acid in reaction, if they exist at all.¹

¹ Aluminum carbonate cannot exist at all. Both the acid and base being weak, hydrolysis takes place with the formation of aluminum hydroxide.

The explanation of the hydrolysis is best given by writing the chemical reactions as follows:



In the first reaction sodium hydrate is highly dissociated, carbonic acid very slightly dissociated into ions, so that the alkaline reaction due to hydroxyl ions predominates.

In the second reaction aluminum hydroxide is not dissociated, while sulphuric acid is highly dissociated, so that the acid reaction due to the hydrogen ions is produced.

Between these two extremes we meet with a very great number of cases of hydrolysis, the principles of which should be understood by all manufacturers of protective paint compounds. In many cases salts and compounds which do not immediately hydrolyze when dissolved in water, will undergo slow decomposition under the action of acid gases and moisture in the atmosphere, and hydrolytic products will be formed. An understanding of these points will frequently explain the stimulative corrosion effects produced by certain types of pigments.

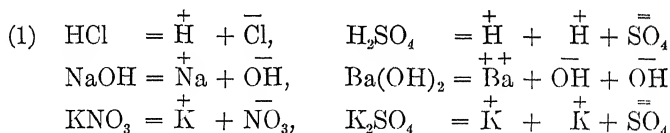
Electrolysis. — The phenomenon known as electrolysis takes place whenever a current of electricity passes through a solution capable of conducting the current. Such a solution is known as a conductor of the second class to distinguish it from an ordinary conductor like a metallic wire, which is of the first class. A solution of sugar will not conduct a current of electricity while a solution of salt will readily do so. This difference in behavior is accounted for by the fact that the salt is dissociated into ions while the sugar is not. A substance which in solution will conduct electricity is known as an electrolyte. The phenomenon of electrolysis shows that when a current is passed through a solution of an electrolyte, there is a mechanical movement of the ions towards the electrodes. Thus, if a current is passed through a solution of hydrochloric acid the positive hydrogen ions will proceed to the negative electrode where they will plate out after giving up their electrical charges. Having now assumed the atomic or gaseous condition, the hydrogen escapes from the system in the form of minute bubbles. While this action is occur-

ring at the negative pole an equivalent amount of chlorine is being plated out and disengaged at the positive pole.

It is not necessary that an outside or external source of electricity should be at work before electrolysis can take place. If two strips of dissimilar metal are plunged part way into a solution and connected by a wire, or by any other means, across the top a current will flow around the circuit. This current is generated at the expense of the more electro-positive metal in the couple. The electro-positive element rapidly shoots off positive ions into the solution, thereby leaving itself negatively charged so that it invariably appears as the negative pole in the circuit. Even two steel needles from the same package are sufficiently dissimilar to show a slight difference of potential when coupled in such a way, and one will be protected while the other suffers accelerated corrosion. *From the standpoint of the electrolytic theory all iron and steel must be thought of as a composite structure, as though, indeed, it was compounded of more or less well consolidated bundles of more or less homogeneous needles or units.* This statement contains the crux of the whole electrolytic explanation of corrosion and will be further developed in another chapter.

Modes of Ion Formation. — Jones describes the various modes of ion formation very clearly in the following paragraphs:¹

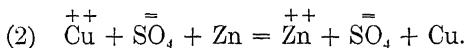
“From what has been said thus far, the impression might be gained that ions can be formed from molecules in only one way — the molecules breaking down directly into an equivalent number of anions and cations. This is one way in which ions are formed, and the way with which we are most familiar, since it occurs most frequently. The following examples illustrate this mode of ion formation:



Another method by which an ion can be formed, is for an atom to take the charge from an ion, converting it into an atom, the original atom becoming an ion. Thus, when a bar of zinc is dipped into a solution of copper salt, the copper which was present

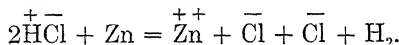
¹ Jones, Elements of Physical Chemistry, loc. cit., pp. 419-421.

in the solution as an ion gives up its two charges to an atom of zinc, becoming an atom; while the zinc, having received the charges, becomes an ion. This is the well-known precipitation of copper from a solution, by zinc. We will call this the second mode of ion formation.



“All that occurs is a transference of electricity from the copper to the zinc. This is exactly analogous to what takes place whenever one metal replaces another, as it is said, from its salts.

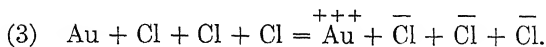
“The replacement of the hydrogen ion from acids by a metal like zinc is an illustration of the same mode of ion formation.



What takes place here is simply the transference of the electrical charge from the hydrogen which does not hold its charge firmly, to the zinc which holds its charge much more firmly than the hydrogen, and, therefore, takes the charge from the hydrogen.

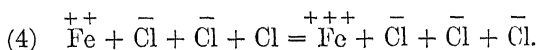
“This is typical of the reaction of acids on metals in general; and is probably typical of *substitution* in general. The work of Thomson makes it highly probable that when substitution takes place in organic compounds, the entering atom or group takes the charge away from the atom or group displaced. The substituting atom or group always has the same charge that the substituted atom or group had when in the compound. *The entire act of substitution is essentially an electrical act, and not a chemical act, as that term is usually understood.* This is true whether we are dealing with the substitution of the hydrogen ions of an acid by a metal, or with substitution in organic compounds.

“Another method of ion formation is where an atom of one substance passes over into a cation, at the same time that an atom of another substance passes over into an anion. When gold is dipped into chlorine water, both the gold and chlorine are in the atomic or molecular condition. But under these conditions the gold can become a cation, and the chlorine can form anions. This we will term the third method of ion formation.



This is usually expressed by saying that gold dissolves in chlorine water.

"The fourth and last method by which ions are formed is where an atom passes over into an ion, at the same time converting an ion already present into one with a different quantity of electricity upon it. Thus, chlorine brought in contact with ferrous chloride in solution forms an anion, at the same time converting the ferrous ion into a ferric ion.



This is an example of what has so frequently been called in chemistry, *oxidation*. The reverse phenomenon is, of course, what has been termed *reduction*. In this sense oxidation is simply increasing the number of charges carried by an ion, and reduction is diminishing the number of such charges.

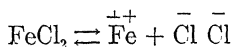
"These four methods of ion formation, which have been so clearly pointed out by Ostwald,¹ include all the cases which are known. If we study them carefully and apply them to chemical reactions, we shall see that they throw much light on many problems in chemistry, the meaning of which has hitherto been concealed in darkness."

Oxidation and Reduction. — The true nature of the processes known as oxidation and reduction, as set forth above, should be thoroughly understood by every student of the problem of corrosion. By valence the chemist means the combining power of a given atom for other atoms, though as has been shown it may be considered as an expression for the measure of the electrical state of the ion. Many of the elements have only one known valence state or combining value, as for instance, hydrogen, which is always univalent and unites with one other univalent atom to form a compound as in hydrochloric acid (HCl). Bivalent elements like calcium unite with two univalent atoms, as in calcic chloride (CaCl₂). Iron is typical of a number of other elements in that it can occur in two states of valence, viz., the ferrous condition in which it is bivalent as in FeCl₂, and the ferric condition in which it is trivalent, as in FeCl₃. Every change from the lower to the higher state is known as oxidation, and every change from the higher to the lower is conversely a reduction.

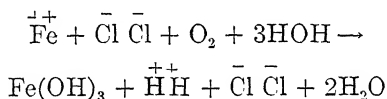
¹ See Lehrb. d. Allg. Chem., II, 786.

A neutral solution of ferrous chloride exposed to the air rusts just as surely as does a moist piece of metallic iron, and it is probable that both actions are due to ionic changes dependent upon the electrical states of the reacting ions.

It is characteristic of ferrous ions that they are in an unstable condition, and in the presence of the oxygen in the atmosphere are changed to the ferric state. A solution of ferrous chloride contains ferrous ions and chlorine ions and may be written thus:



If we admit no more chlorine ions to the system, as the change from the ferrous to ferric states goes on hydrolysis takes place and finally in the course of time a reddish rust consisting of ferric hydroxide will make its appearance.



Ferric¹ hydroxide is an insoluble compound so that when it is formed it drops out of solution. This action of dropping out of solution is known to chemists as precipitation, and the result of such action is called a precipitate. It is at once evident that such a precipitation removes a certain amount of material from the solution system, and thereby alters the equilibrium between solution pressure and osmotic pressure, as has been previously explained.

Now if we apply these same principles to the discussion of the simple system represented by the immersion of a piece of iron in pure water, the rust which forms can be easily and simply accounted for. Iron has a definite solution tension in pure water, especially at certain points on its surface, which are electro-positive to other points or areas.² The iron here enters the solution as positive ferrous ions, the corresponding negative charges being assumed by hydroxyls. But immediately the oxygen of the air

¹ As a matter of fact ferric hydroxide cannot be properly expressed by a chemical formula such as $\text{Fe}(\text{OH})_3$. It appears as a colloidal precipitate of indefinite composition as far as the amount of water associated with it is concerned. It would be more appropriately written as $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ but, for the purpose of the present discussion this point may be overlooked.

² Compare p. 17 and illustration, Fig. 5.

changes the ferrous ions to the ferric condition resulting in the hydrolytic formation of the insoluble ferric hydroxide or rust. The more detailed discussion of the electrolysis which takes place will be taken up in a later chapter.

Electrolysis and Polarization. — When a metal electrode is immersed in an electrolyte it tends to dissolve, or in other words, to pass from the atomic to the ionic condition. This is known as electrolytic solution pressure. As the atom of metal passes into solution it assumes a positive charge of electricity which it must take from some source. If the electrolyte contains positive hydrogen ions, that is to say, if the electrolyte is acid, the entering metallic ions will acquire their charges by exchange with hydrogen, which immediately leaves the system in the form of minute gaseous bubbles. If the electrolyte is neutral the metallic ions take their positive charges from the electrode which is thereby left negatively charged. In almost neutral media a combination of the two results may take place, the hydrogen being disengaged too slowly to be visible.

Such a state of affairs leads to a polarization effect first described by Helmholtz¹ and called by him an electrical double layer. The positively charged metallic ions cannot escape or free themselves from the negatively charged surface, although there is sufficient pressure to prevent the reneutralization of the charges. This effect polarizes the surface, which for practical purposes may be considered as plated with positive ions. Walker² describes this phenomenon in the following words:

“Every metal when placed in water, or under such conditions that a film of water may condense upon it, tends to dissolve in the water, or, in other words, to pass from its atomic or metallic condition into its ionic condition. This escaping tendency of the metals varies from that shown by sodium or potassium, which is so great as to cause instant and rapid decomposition of the metal and water, to gold or platinum where such tendency to dissolve is zero. Between these two extremes we find the other common metals, including thereunder the element hydrogen, which may be considered as a metal. As the atom of metal passes into the water, it assumes a positive charge of electricity, leaving the metallic mass from which it separated charged nega-

¹ Wied. Ann., 7, 337 (1879).

² Jour. Iron & Steel Inst., I, 70 (1909).

tively; this property or escaping tendency of the metal is termed its solution pressure. It is obvious, however, that this action can continue for only a short time; owing to the fact that the mass of metal and solution are of opposite polarity, the electrolytic tension becomes so great that no more atoms can escape to the ionic state, and the solvent action ceases. This condition was first described by Helmholtz, and called by him an electrolytic double layer. If now there be in the water ions of another metal which has a smaller solution pressure than the one under consideration, the action as above described will be reversed and the ion with the less solution pressure will pass back to the metallic state, plating out on the first metal and giving up its charge of electricity. At this point the first metal will be charged positively, and the solution in the immediate vicinity negative, and there will tend to be set up a second electrolytic double layer opposite in polarity to the first. The result is, a current of electricity flows from the metal to the solution at the point where the metal passes into solution, through the solution to the metal at the point where the ions of the second metal are plating out, and back through the first metal to the starting-point again. The electrolytic double layers are thus destroyed, an electric current passes, and the solvent action of the water on the first metal continues.

"This phenomenon and its relation to the corrosion of iron are clearly exemplified in the well-known Daniel or gravity cell.

"In the case of pure iron in water a perfectly analogous condition is found to exist. Water itself is dissociated to a small but perfectly definite extent into its ions, hydrogen (H), and hydroxyl (OH). When a strip of pure iron comes into contact with water, it sends into the water iron atoms in the form of positively charged ions. Hydrogen as a metal has a much smaller solution pressure than iron, and hence an equivalent number of hydrogen ions plate out on the iron strip (leaving the free hydroxyl ions with their negative charges to balance the iron ions with their positive charges), and an electric current flows from the iron by means of the iron ions to the solution, and by means of the hydrogens from the solution back to the iron again, thus completing the circuit. But here comes an important break in the analogy of the film of copper in the Daniel cell. Deposited copper is a good conductor of the current, and offers no resistance

to its flow from the solution to the iron on which it is attached. The reverse is true of the deposited hydrogen; here we have a high insulator — a film of gas which offers a great resistance to the flow of the current. Hence, although in the case of the iron strip in water all the conditions for continuous solution are present, owing to the resistance offered by the deposited hydrogen film (called polarization) the action must cease.

“Just as in the case of iron in a copper sulphate solution the rapidity of the action depended upon the number of copper ions present in the solution, so here the solution of the iron, in the first instance, depends upon the number of the hydrogen ions present. This number of hydrogen ions, or the concentration of these ions, is increased by the addition of any acid. So weak an acid as carbonic increases the number, but to a relatively small amount; while a strong acid, like hydrochloric or sulphuric, adds to the number to such an extent that the solvent action becomes violent, and the deposited hydrogen comes off as a stream of gas.”

*The Passive State of the Metals.*¹ — It is well known that under certain conditions iron and some other metals assume a condition in which they no longer have all the properties they usually possess. Iron which has been dipped in certain strong oxidizing agents no longer exhibits a solution pressure when dipped into dilute electrolytes, and comports itself as though it were a noble metal. This was first noticed by Keir, a British chemist, as early as 1790.² He found that specimens of bright steel which had been dipped into strong fuming nitric acid became passive and were no longer soluble even in dilute acid, or able to exchange places with copper when dipped into a dilute solution of copper sulphate. Other strong oxidizing agents, especially chromic acid and its soluble salts, have been found to induce this condition of passivity on the surface of iron. This fact has been made the subject of special study by one of the authors, the results of which will be detailed in a later chapter. Since the phenomenon of passivity is produced only by strong oxidizing agents or by galvanic contact which causes oxygen to separate on the surface of the iron, it was explained by Faraday, Wiederman, and

¹ For the bibliography and an excellent discussion of the passive state see Byers Jour. Am. Chem. Soc., 1908, 30, 1718.

² Phil. Trans., London, 1790, 359.

others¹ as due to a thin oxide film. Another explanation is that the passivity of iron is due to a polarization effect produced by the separation and retention of oxygen on the surface of the metal.

Keir² observed that polished iron which had been immersed in red fuming nitric acid was altered in some manner so that its power of precipitating silver and copper from their solutions was inhibited, and this occurred, in the discoverer's own words, "without the least diminution of metallic splendour or change of color." Mugdan³ discussed the passivity acquired by iron which was immersed in fuming nitric or sulphuric acids and concluded that it was not due to the formation of an oxide film, but was a true passivity in the sense of an ennobling (Veredlung) of the metal, accompanied by a low electrical potential. Jones⁴ has discussed the subject in the following words: "A number of attempts have been made to explain the passivity of the metals. Faraday⁵ and Schönbein explained the passivity in the case of iron, as due to the formation of a layer of oxide on the surface of the metal. This was natural when we consider that iron is rendered passive by strong oxidizing agents, and loses its passivity when heated in a reducing gas.

"The oxide layer theory of passivity is now regarded as untenable, since the passive state has been brought about under conditions where oxidation is impossible; and further, has been destroyed under conditions where any layer of oxide if formed would not be disturbed.

"The same fate has befallen the theory that passivity is due to the formation of a protective layer of gas over the surface of the metal. The two views of passivity that have acquired the greatest prominence are those of Finkelstein⁶ and Hittorf.⁷ According to the former, active iron is bivalent and passive iron trivalent. This conclusion was based upon the difference in potential between iron electrodes and the iron salt in which they were immersed. The potential difference depends upon whether the iron salt is in the ferrous or in the ferric conditions.

¹ Dammer's Anorg. Chem., 1893, V. 3, p. 294.

² *Ibid.*

³ Ztschr. Elektrochemie, 1903, 9, 454.

⁴ Jones, El. Phys. Chem., p. 411.

⁵ Phil. Mag. (3), 9, 53 (1836); 10, 175 (1837).

⁶ Ztschr. Phys. Chem., 39, 91 (1901).

⁷ *Ibid.*, 30, 481 (1899); 34, 385 (1900).

"Hittorf also points out that in the case of chromium the passive condition corresponds to the highest valence, and the active to the lower valence. He thinks that we have to do with two allotropic modifications of the elements, one of which is active and the other not."

In spite of these various explanations of the interesting and extraordinary phenomenon of passivity, its fundamental cause is not thoroughly understood and is still an open question. It is possible that plating out of oxygen and a change of valence of the surface ions takes place simultaneously. Whatever the cause, however, the condition of passivity has an important bearing on the problem of the protection of iron and steel, and will be taken up for further discussion later on.

The Electro-chemical Series of the Metals. — If a strip of iron is plunged into a solution of a salt of copper, iron will go into solution and copper will plate out. This is because iron is electro-positive to copper, or, in other words, iron has a higher solution pressure than copper. The copper ions in solution give up their positive charges of electricity to the iron, which in turn assumes the ionic condition. If now a strip of iron is plunged into a solution of a salt of zinc no such phenomenon takes place because iron is electro-negative to zinc, and it is only when a strip of zinc is plunged into a solution of an iron salt that exchange can take place. If two metals are connected together in metallic contact to form a couple and are then plunged into a dilute solution of an electrolyte, the more electro-positive metal will dissolve and oxidize (rust), while the more electro-negative will be practically speaking unacted on. In the meantime current will flow around the circuit. This is the underlying principle of all galvanic action and explains the action of all primary batteries. In the following list a number of the more familiar metals are put down in the order of their diminishing solution tensions, and this may be termed a tension series.

Magnesium	Nickel
Zinc	Lead
Aluminum	Copper
Cadmium	Tin
Iron	Antimony

A metal anywhere in the above series will tend to precipitate, from a solution of its salts, a metal lower in the series. Thus

zinc and iron will precipitate copper. A metal at any point when coupled with another lower in the series and plunged into a corroding medium will throw off positive ions into solution, and thereby become the negative pole. Zinc is the negative pole in almost all the common types of primary batteries. It is apparent from this that if metals which stand below iron are successfully used as protective coatings it is because they have very low solution tensions. It is equally apparent why pinholes or cracks in a tin or copper coating will result in more rapid corrosion of the exposed portions of the iron. These points must await further discussion in a later chapter; it should at once be stated, however, that the electro-chemical state of a metal may be considerably modified by the presence of other metals which may be alloyed with it. This is an important point which is often overlooked in connection with the problem of protecting iron from corrosion. Thus zinc which is strongly electro-positive to iron is much used as a protective coating. There are, however, certain alloys of zinc with iron, which are said to be electro-negative to iron, and as these alloys may be formed in the spelter baths of the hot dip process, much of the zinc coating which is turned out in metallurgical processes may have quite the opposite effect from the one desired.

*The Theory of Indicators.*¹ — Certain substances usually of an organic type when dissolved in water are observed to change color when the reaction changes. Thus, a solution of litmus, which shows red in an acid solution, will change to blue in an alkaline solution. The color change is dependent upon the degree and state of the electrolytic dissociation of the compounds. Substances which undergo these delicate changes are known as indicators. The only one of these which will be referred to in this work is phenolphthalein, and for the benefit of many persons who are interested in the corrosion problem, but who are not familiar with the theory of indicators, the following explanation is included. Phenolphthalein shows the presence of hydroxyl ions in a solution by the formation of a pink color, thus indicating

¹ It is fair to state that the explanation of the action of indicators based on the theory of electrolytic dissociation is not universally accepted by chemists. The principle, however, remains the same, even if a better explanation can be advanced, for the pink color developed by phenolphthalein will always furnish a sensitive indication of the negative pole in an electrolytic circuit.

an alkaline reaction. Phthalic acid was first prepared by Laurent in 1836, by the oxidation of naphthalene, and was first called naphthalinic acid. It was afterwards shown that the compound was not directly related to the naphthalene structure, and Laurent changed the name to phthalic acid, the derivatives of which became known later as phthaleins. Phenolphthalein is a product which is formed by the condensation of two molecules of phenol or carbolic acid with the anhydride of phthalic acid. It is in its nature so weak an acid that it is not dissociated in solution, and as the molecule is colorless no color is seen when it is added to a perfectly neutral solution. If, however, an alkali is added the corresponding salt of the weak acid is formed, which immediately dissociates with the formation of a colorless metallic cation, and the strongly rose-colored organic anion. Thus all hydroxides of basic elements will show the pink color in solution, even when present in only the slightest excess. On this account phenolphthalein is an exceedingly delicate indicator of the presence of hydroxyl ions.

Phenolphthalein as an Indicator of the Presence of Electrolysis.

— As hydroxyl ions are always found in more or less excess around the negative pole of a galvanic circuit after the positive hydrogen ions have neutralized their charges and disappeared, phenolphthalein can be used as an indicator of the existence of a negative pole. In order to show the sensibility of this substance for indicating an excess of hydroxyl ions by the development of a distinct pink color, the following simple experiment has been described:¹

Five hundred and fifty c.c. of distilled water containing 1 c.c. of phenolphthalein indicator was boiled down in a Jena flask to 500 c.c. One one-hundredth normal potassium hydroxide solution was then run into the quickly cooled water from a burette. It was thus found that about 1 c.c. of one one-hundredth normal potassium hydroxide was the limit of the quantity necessary to produce a distinctly visible pink color; 1 c.c. of one one-hundredth normal potassium hydroxide contains 0.00017 gram of hydroxyl. This quantity in 500 c.c. of water represents a concentration of about 0.35 part of hydroxyl per million.

This experiment shows how extremely delicate the phenolphthalein test is as an indicator of the presence of hydroxyl ions, and hence of the negative pole in an electrolytic circuit.

¹ Cushman, Bull. 30, Office Public Roads, U. S. Dept. Agr.

Colloids and Crystalloids. — Before closing this chapter on solutions, a brief reference should be made to the condition of substances as they precipitate out of solution, as a general knowledge of the subject will be of assistance in the design and preparation of inhibitive compounds. The action of colloids under the effects of electrolysis will also be found later to have a bearing on the corrosion problem.

Electro-Chemical Properties of Colloids. — Whenever substances suddenly precipitate out of solution they appear either in a finely crystalline condition in which they are denominated crystalloids, or in a gummy, gelatinous, more or less coagulated condition, as the case may be, in which we define them as colloids, or colloidal precipitates. It will not be necessary here to give a full description of the properties of colloids in general, as this information can be obtained from any complete text-book on physical chemistry. The points that particularly interest us in this work are the peculiar absorbent powers of colloidal precipitates and their electro-chemical properties. Many colloidal precipitates are dried and used as pigments, and such substances not only absorb considerable quantities of water, but also absorb and carry down with them impurities from the mother liquors or solutions from which they were precipitated.

There seems to be satisfactory evidence that colloidal precipitates in suspension in an electrolyte carry electrical charges just as ions do. This is shown by the fact that the colloidal particles when suspended in a solution migrate to the electrodes under the influence of electrolysis. Colloidal ferric hydroxide, which although not exactly is essentially similar to all freshly formed iron rust, moves with the current to the cathode, this peculiarity it shares with all basic hydroxides. Acid hydroxides like precipitated silicic acid move in the opposite direction. The ferric hydroxide is therefore charged positively and the silicic acid negatively. This property appears to be a general one for all colloidal suspensions, and seems, under certain conditions, to give them the tendency of absorbing from the solution ions of opposite sign. According to Jones, two theories have been proposed to account for the electrification of the colloid particles. According to one of these theories, the particles of the colloidal precipitates assume the charge of one sign while the surrounding water takes on the charge of the other sign. This explanation

does not seem to be in accord with the observed facts, and the more probable theory is that from every colloidal aggregate there split off either positive or negative ions, leaving the residue of the aggregate carrying the opposite charge. Thus, basic hydroxides would split off hydroxyl ions, and the residue be charged positively; in the same way silicic acid would split off hydrogen ions, leaving the colloidal residue charged negatively.¹

This absorbent tendency of colloidal precipitates, both for water and salts, as well as their electro-chemical properties, should be thoroughly understood by paint technologists who are studying the protection of iron and steel. The explanation of the stimulating effects produced by certain pigments which are theoretically inhibitors is usually furnished by these colloidal absorptions which take place in the course of manufacture of the pigments.

Conclusion of the Chapter. — It is hoped that a careful reading and study of this chapter by metallurgists and others interested in the special problems with which this book deals will lead to a clearer understanding of the discussion and data which is included in succeeding chapters. It is not necessary that the reader should be a chemist in order to understand the explanations which have been presented, and it is hoped that those who have never studied even the rudiments of chemistry and electrical action will have been introduced to theories which are further developed in succeeding chapters. In conclusion, the authors desire to state that they are conversant with the interesting generalizations of Kahlenberg² and his school, who do not accept the theory of solutions, and who have brought strong arguments, based on experimental evidence, to bear against it. Nevertheless, the theory has been and still is a useful one whatever its ultimate fate may be; the authors are strong in the conviction that the theory of solutions expresses fundamental truth even if it must eventually be modified in form.

¹ Jones, *El. Phys. Chem.*, p. 283.

² See *Science*, XXXI, 785, 41.

CHAPTER III

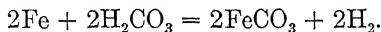
THE THEORY OF CORROSION

The Three Theories which have been Advanced to Explain Corrosion.— Three separate theories which, though they all more or less overlap, nevertheless involve distinctly different reactions, have been advanced and strenuously defended in the effort to furnish an explanation for the rusting of iron. These may be stated as the carbonic-acid, the hydrogen-peroxide, and the electrolytic theories.

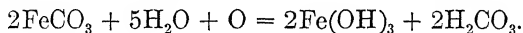
Before any distinct progress can be made in the manufacture of metal that shall be more than ordinarily resistant to corrosion, it is of great importance that the underlying causes of oxidation should be clearly understood. It is the object of this chapter to discuss the different theories and to present certain evidence which bears directly upon the subject.

*The Carbonic-acid Theory.*¹— The carbonic-acid theory is the one which until recently was most generally held. The theory presumed that without the interaction of carbonic or some other acid the oxidation, or better, the hydroxylation, of iron cannot take place. The theory is best set forth in the words of a textbook recently published.²

“The process of rusting is a cyclical one, and three factors play an important part: (1) An acid, (2) water, (3) oxygen. The process of rusting is always started by an acid (even the weak carbonic acid suffices); the acid changes the metal to a ferrous salt with evolution of hydrogen:



“Water and oxygen now act upon the ferrous salt, causing the iron in this salt to separate out as ferric hydroxide, setting free the same amount of acid which was used in forming the ferrous salt:



¹ The best presentment of the general acid theory is due to Friend, Jour. Iron and Steel Inst., 77, 5, 1908.

² Treadwell and Hall, Analytical Chemistry, 1907, p. 92.

"The acid which is set free again acts upon the metal, forming more ferrous salt, which is again decomposed, forming more rust. A very small amount of acid, therefore, suffices to rust a large amount of iron. If the acid is lacking, the iron will not rust. If we desire to prevent this rusting, we must neutralize the acid, *e.g.*, add milk of lime. Iron remains bright under an alkali."

Corrosion Occurs when Carbonic Acid is Absent. — Although the above explanation is sufficiently plausible, and in spite of the fact that carbonic acid, as well as other acids, does act a part in the ordinary rusting of iron, it will presently be shown that iron readily oxidises, not only when carbonic acid is entirely absent, but also in dilute alkaline solutions. It is only when the hydroxyl ions supplied by an alkaline solution have reached a certain concentration that rusting is entirely prohibited.

The carbonic-acid theory was founded originally on the investigations of Crace Calvert,¹ as interpreted by Crum Brown.² It has also more recently been vigorously defended by Moody,³ who insists that with water and oxygen quite free from carbonic acid iron cannot rust. This view is, however, not shared by Dunstan, Jowatt, and Goulding,⁴ or by Whitney⁵ or Cribb,⁶ all of whom give experimental evidence to show that rusting takes place rapidly in the absence of carbonic acid, provided liquid water and oxygen are present. The experiment of Dunstan and his coworkers was so carefully carried out that there seems to be no doubt that if carbonic acid plays any role whatever it is an unimportant one, and that rusting can go on with extreme rapidity in its absence.

In order to confirm this conclusion the following experiment was made by one of the writers:

The Jena glass flasks A, B, and the beaker C, shown in Fig. 6, were nearly filled with freshly distilled water and boiled vigorously for one-half hour. While the boiling was still proceeding bright polished strips of charcoal iron and steel were slipped into flasks A and B, and the rubber stoppers, which had been previously

¹ Manchester Lit. Phil. Mem., 1871, 5, 104.

² Jour. Iron and Steel Inst., 1888, 129-131.

³ Proc. Chem. Soc. (Lond.), 1906, 22, 101.

⁴ Jour. Chem. Soc. (Lond.), 1905, 87, pt. 2, 1548.

⁵ Jour. Am. Chem. Soc., 1903, 25, 394.

⁶ The Analyst, 1905, 30, 232.

cleaned by prolonged boiling in pure water, tightly inserted. After boiling for fifteen minutes longer the clamp at the end of tube D was opened for a moment and the back pressure allowed to drive any last traces of air from the tube. After tightly closing the clamp again, the lamps under flasks A and B were removed while the water in C was still kept boiling. Boiled water immediately sucked back until the whole apparatus was completely filled, no trace of air being present. At all events, no slightest trace of rust appeared on the bright metal strips when kept indefinitely under this boiled water. Pure oxygen from a cylin-

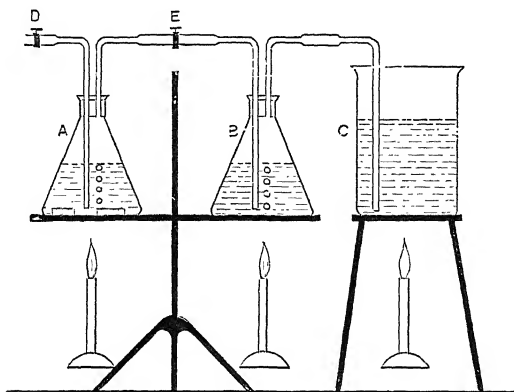


FIG. 6. — Apparatus to show the action on iron of pure water and oxygen.

der was now washed perfectly free from last traces of carbonic acid by passing the gas through a train of wash bottles containing caustic potash, barium hydroxide, and lime water. On allowing this carefully purified oxygen to enter at D and bubble through the system of flasks, rust appeared on the bright metal surfaces in five minutes or less and in one hour had become deep and heavy. The action, just as in Dunstan's experiments, did not take place evenly all over the surface, but in patches, which had the appearance of a more or less regular pattern following the physical structure of the metal. This experiment has been frequently repeated, with every possible precaution to avoid the entrance of even the smallest trace of carbonic acid. On numerous occasions a few drops of phenolphthalein indicator was added to the boiling water in the three flasks, and invariably a pink color

developed, proceeding from the metallic surfaces. This effect will be discussed at length further on and is mentioned at this place as contributory evidence that carbonic acid is not necessarily present, as Moody believes, before any reaction between iron, water, and oxygen can take place.

If pure, dry carbonic acid gas, freed from oxygen by passing through several wash bottles containing pyrogalllic acid dissolved in sodium bicarbonate solution, was substituted for the pure oxygen gas and allowed to enter through tube D, no perceptible action took place on a bright piece of steel after several hours, although there can be no doubt that iron passed to a slight extent into solution as ferrous carbonate. Finally, if pure oxygen was allowed to enter at the same time and mingle with the carbonic acid, corrosion began in a short time. There was, however, a difference in the appearance of the rust that was formed with and without the interaction of carbonic acid. In the presence of carbonic acid the characteristic blue-green gradually changing to the red color peculiar to rust was observed. This appearance invariably accompanies the early stage of attack when iron is rusting in the presence of carbonic acid. In the experiments in which pure oxygen alone was permitted to enter the apparatus the blue-green initial stage of oxidation was never observed, the red ferric hydroxide making its appearance from the first, as it usually does, in normal cases of atmospheric rusting of bright iron surfaces.¹

It may be doubted whether it is possible to boil out all carbonic acid from the water contained in the apparatus shown in Fig. 6. Granting that this is the case in regard to last traces, it is easily shown that the hydrogen ions which would be supplied by a minute quantity of carbonic acid are of no more importance than the hydrogen ions supplied by the normal dissociation of pure water, and that the assumption that carbonic acid must be present is quite unnecessary. Whitney² shows this very clearly in the following paragraph:

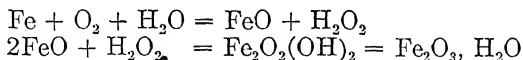
¹ Statements frequently appear in discussions of the corrosion problem in regard to the importance of analyses of various samples of iron rust. As a matter of fact little can be learned from such analyses. The ferroso-ferric hydroxides, carbonates, etc., that are formed are of indefinite composition and their chemical constitution throws little if any light on the mechanism of the corrosion reactions.

² Jour. Am. Chem. Soc., 1903, 25, 397.

“Assuming the laws of Henry and Dalton to apply to the solubility of carbonic acid gas in water, also that the solubility of the pure gas under ordinary pressure is one volume for one volume of water (which is correct at 15° C.), and, finally, that the normal content of carbonic acid in the atmosphere is 2 parts in 10,000 by volume, we should expect water in equilibrium with air containing this concentration of carbonic acid to contain 0.0002 volume carbon dioxide per volume of water. This corresponds to a concentration of the carbonic acid equal to 0.00001 mol per liter, or 0.00002 normal. From the dissociation constant 3040×10^{-10} determined by Walker,¹ it follows that the first hydrogen of the acid is 16 per cent. dissociated at this concentration. From this it follows that 10,000,000 liters of water containing carbonic acid in equilibrium with ordinary air at 15° contains 16 grams of hydrogen ions, or only 16 times as many as perfectly pure water contains. At the boiling temperature the carbon dioxide dissolved would probably yield a concentration of hydrogen ions even less than in pure water, for not only is the solubility of the gas greatly diminished, but the dissociation of water is greatly increased by rise of temperature. Moreover, the distilling water would rapidly reduce the concentration of any carbonic acid capable of dissolving in water at 100° C.”

The carbonic acid theory does not furnish a complete explanation of the phenomenon of corrosion, but it does express partial truth inasmuch as hydrogen ions must be present before the attack on the surface of iron can be made. The fact as brought out in the previous paragraph that even pure water provides a sufficient number of hydrogen ions to start the action shows that the role of carbonic acid is only contributory and not the sole cause.

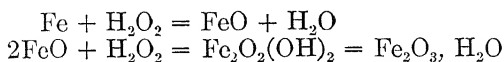
The Peroxide Theory of Corrosion. — The peroxide theory of corrosion has not been found in accordance with observed facts, but it will be briefly stated here for the sake of completeness. This theory is based on the well-known scheme of oxidation processes advanced by Traube.² Thus the chemical reactions concerned in the formation of iron rust should be written:



¹ Zts. Phys. Chem., 1900, 32, 137.

² Ber. d. chem. Ges., 18, 1881.

The excess of hydrogen peroxide immediately reacts with the iron, forming a further quantity of rust:



One of the arguments which was used by its supporters to strengthen the theory was the seemingly extraordinary but now well-known fact that iron cannot rust in solutions of certain strong oxidizing agents, such as chromic acid and its salts. As chromic acid is known to destroy hydrogen peroxide, the explanation on first thought seems reasonable. The theory also seemed to derive some confirmation from the fact that delicate tests for hydrogen peroxide have been obtained during the slow oxidation of zinc and some other metals. On the other hand, in the case of iron these same delicate tests obstinately refuse to reveal even its transitory presence during the ordinary process of rusting. The theory has been criticised by Divers,¹ Moody,² and Cribb,³ — the first named having pointed out that it is not tenable to argue that, because such substances as chromic acid and alkalis gradually destroy hydrogen peroxide, they must prevent its formation. For instance, ferrous sulphate is oxidized by free chlorine, but it does not prevent manganese dioxide and hydrochloric acid from reacting when brought together in its presence. Moreover, if the formation of hydrogen peroxide was a necessary stage in the rusting of iron, and this is inhibited by certain substances which destroy hydrogen peroxide, why is not the inhibition extended to strong reducing agents generally? The theory is an interesting and suggestive one, but in the author's opinion is not supported by the facts.

The Electrolytic Theory. — ~~From~~ From the standpoint of the modern theory of solutions, all reactions which take place in the wet way are attended with certain readjustments of the electrical states of the reacting ions. The electrolytic theory of rusting assumes that before iron can oxidize in the wet way it must first pass into solution as a ferrous ion. The subject has been interestingly treated by Whitney,⁴ who discussed it from the standpoint

¹ Proc. Chem. Soc. (Lond.), 1905, 21, 251.

² Jour. Chem. Soc. (Lond.), 1906, 89, 90, 720.

³ Analyst, 1905, 30, 225.

⁴ Loc. cit., p. 38.

of Nernst's conception of the source of electro-motive force between a metal and a solution. When a strip of metallic iron is placed in a solution of copper sulphate, iron passes into solution and copper is deposited, this change being of course accompanied by a transfer of electrical charge from the ions of copper to those of iron. Hydrogen acts as a metal and is electrolytically classed with copper in relation to iron. If, therefore, we immerse a strip of iron in a solution containing hydrogen ions, an exactly similar reaction will take place, iron will go into solution, and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron, and, therefore, its subsequent oxidation, must be accompanied by a "precipitation" or setting free of hydrogen. It is very well known that solutions of ferrous salts as well as freshly precipitated ferrous hydroxide are rapidly oxidized by the free oxygen of the air to the ferric conditions, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one.

Pure Water a Solvent of Iron. — As iron has been shown by Whitney, Dunstan, and one of the authors, to rust in the presence of pure water and oxygen alone, the electrolytic theory as a fundamental cause of the wet oxidation of iron must stand or fall on the determination of one crucial question, viz.: Does iron pass into solution, even to the slightest extent, in pure water? If iron does dissolve, the electrolytic theory is so far satisfactory; if it does not dissolve, we must conclude that the oxygen finds some way of directly attacking the metal.

Almost every one will admit that in the case of impure iron, with its unhomogeneous physical and chemical constitution, electrolysis will supervene, but it must be remembered that we are now concerned with the underlying cause of the wet oxidation or hydroxylation of iron, regardless of its state of chemical purity.

According to the dissociation theory, even the purest water contains free hydrogen ions to the extent of about 1 gram in 10,000,000 liters. If iron dissolves in the purest water it should be by interchange with hydrogen, and as Whitney¹ has pointed out, pure water is to this extent an acid. In order to get experimental evidence on this crucial point, Whitney describes the following experiment:

¹ *Loc. cit.*, p. 38.

"A clean bottle was steamed out for a time to remove soluble alkali from the glass and was then filled with pure distilled water, which was kept boiling by passing steam through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80°C. , and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid, and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy and assumed a yellow color. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide."

In order to obtain more light on the subject one of the writers devised the following experiment, which is sufficiently simple to be repeated by any one without encountering any difficulties whatever. The apparatus used is shown in Fig. 7.

The two clean Jena glass flasks A and B are three-quarters filled with pure freshly distilled water. Two drops of an alcoholic solution of phenolphthalein indicator (1 gram in 100 c.c. pure alcohol) are added to the water in each of the flasks. The beaker C is more capacious than the flasks A and B. The flasks D and E are used in each experiment as blanks to check the results obtained. After connecting up as shown, the water in each vessel is simultaneously boiled very vigorously until about one-quarter is boiled off. The rubber stopper in A is then lifted, and clean, polished strips of iron quickly slipped in. The stopper is again tightly inserted and the boiling continued for about fifteen minutes.

The lamps under A and E are then extinguished, while the water in B, C, and D continues to boil. As soon as flasks A and E have sucked back boiling water so that they are completely filled, the lamps under flasks B and D are also extinguished. When B is quite full, flasks A and B are quickly cooled by surrounding them with cold water. The valve at F is then closed. By this means the bright specimens are immersed in water practically free from air, oxygen, or carbonic acid, and may be kept under observation for any desired length of time. This experiment has been repeated a great number of times with different samples of iron and steel, and no rusting has ever been observed unless air was allowed to enter.

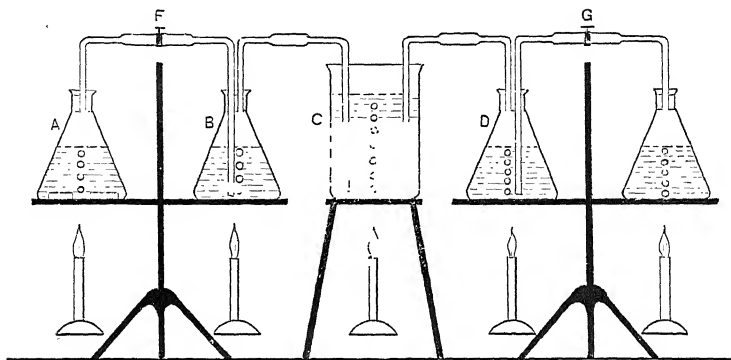


FIG. 7. — Apparatus to determine the extent of the solubility of iron in pure water.

It has been shown that the electrolytic theory of the wet oxidation of iron is based on the premise that iron must first go into solution, an equivalent amount of hydrogen being set free. The resulting ferrous hydroxide in solution betrays its presence by producing a pink coloration with the phenolphthalein indicator. In every experiment made the pink color was seen, although in some cases the color developed slowly and only after the lapse of a number of hours. That the color was not due to the action of the water on the Jena glass was shown by the fact that no color appeared on the blank side of the experiments.

Since it was thought that some doubt might be felt whether even the small amount of phenolphthalein present could attack the iron, the experiment was repeated with iron and boiled water

alone, but the results invariably showed that a small amount of iron had dissolved. In view of the ease with which these experiments can be confirmed, it would seem needless to yield more space to this phase of the discussion. It appears to the writer to be demonstrated that Whitney was right in his assertion that iron goes into solution up to a certain maximum concentration in pure water, without the aid of oxygen, carbonic acid, or other reacting substances.

Rusting of Iron Primarily due to Attack by Hydrogen Ions. — This point established, it becomes apparent that the rusting of iron is primarily due, *not to attack by oxygen, but by hydrogen ions*. Absolute confirmation of this view will be given later on.

In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every iron ion that appears at a certain spot demands the disappearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyl ions inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarizing or dampening effect which prevents the solution of iron and the separation of hydrogen. This will be more fully discussed later on.

Brief Explanation of Corrosion of Iron, from Standpoint of Electrolytic Theory. — From the standpoint of the electrolytic theory, the explanation of the corrosion of iron is not complicated, and so far has been found in accordance with all the facts. Briefly stated, the explanation is as follows: Iron has a certain solution tension, even when the iron is chemically pure and the solvent pure water. The solution tension is modified by impurities or additional substances contained in the metal and in the solvent. The effect of the slightest segregation in the metal, or even unequal stresses and strains in the surface, will throw the surface out of equilibrium, and the solution tension will be greater at some points than at others. The points or nodes of maximum solution pressure will be electro-positive to those of minimum pressure, and a current will flow, provided the surface points are in contact,

through a conducting film. If the film is water, or is in any way moist, the higher its conductivity the faster iron will pass into solution in the electro-positive areas, and the faster corrosion proceeds. Positive hydrogen ions migrate to the negative areas, negative hydroxyls to the positives. As explained in a previous chapter, by a hydrogen ion is meant a dissociated hydrogen atom carrying its equivalent static electrical charge, which may be represented by the symbol $\overset{+}{\text{H}}$. The hydroxyl ion is written OH^- . Water, which may be expressed by the symbol HOH , is made up of the dissociation products $\overset{+}{\text{H}}$ and OH^- . An acid like hydrochloric acid (HCl) dissociates into $\overset{+}{\text{H}}$ and Cl^- . An acid is always highly dissociated in solution, while water itself is only slightly dissociated. This explains why the presence of an acid increases the concentration of the hydrogen ions. Ionization always takes place in every solution of an inorganic compound, and even the purest water is slightly dissociated into its constituent ions $\overset{+}{\text{H}}$ and OH^- . The more ionized a solution is, the higher its electrical conductivity, and the more rapid the damage to the underlying iron.

If the concentration of the hydrogen ions is sufficiently high, which, as has been shown, is only the same as saying if the solution is sufficiently acid, the hydrogen ions will exchange their electrostatic charges with the iron atoms sweeping into solution, and gaseous hydrogen is seen escaping from the system. This takes place whenever iron is dissolved in an acid. If, however, as is usual in ordinary rusting, the acidity is not high enough to produce this result, the hydrogen ions will polarize to a great extent around the positive nodes without accomplishing a complete exchange, and the so-called electrical double layer of Helmholtz will be formed.¹ This polarization effect resists and slows down the action. Nevertheless, although it cannot be seen, some exchange takes place and iron slowly pushes through, as is shown by the development of the blue nodes in the ferroxyl test. For every exchange of static charge between iron and hydrogen at the positive node, a corresponding negative hydroxyl ion appears at the negative node which is shown in pink with the ferroxyl indica-

¹ Wied. Ann., 1879, 7, 337.

tor. In other words, as fast as the iron sweeps into solution the concentration of ferrous hydroxide grows, but the ferrous reaction appears in one place and the hydroxyl in another. It is now that the oxygen of the atmosphere dissolved in the solution takes up its work, the ferrous ions are oxidized to the insoluble ferric condition, which results in the precipitation of rust, and the action of hydrolysis proceeds. The formation of the insoluble ferroso-ferric carbonates and hydroxides, changing to the red ferric hydroxide known as rust, is familiar to every one.

W. H. Walker puts into the following words a very similar explanation of the action which takes place:¹

"Every metal when placed in water, or under such conditions that a film of water may condense upon it, tends to dissolve in the water, or, in other words, to pass from its atomic or metallic condition into its ionic condition. This escaping tendency of the metals varies from that shown by sodium or potassium, which is so great as to cause instant and rapid decomposition of the metal and water, to gold or platinum where such tendency to dissolve is zero. Between these two extremes we find the other common metals, including thereunder the element hydrogen, which may be considered as a metal. As the atom of metal passes into the water, it assumes a positive charge of electricity, leaving the metallic mass from which it separated charged negatively; this property or escaping tendency of the metal is termed its solution pressure. It is obvious, however, that this action can continue for only a short time; owing to the fact that the mass of metal and solution are of opposite polarity, the electrolytic tension becomes so great that no more atoms can escape to the ionic state, and the solvent action ceases. This condition was first described by Helmholtz, and called by him an electrolytic double layer. If now there be in the water ions of another metal which has a smaller solution pressure than the one under consideration, the action as above described will be reversed and the ion with the less solution pressure will pass back to the metallic state, plating out on the first metal and giving up its charge of electricity. At this point the first metal will be charged positively, and the solution in the immediate vicinity negative, and there will tend to be set up a second electrolytic double layer opposite in polarity to the first. The result is, a current of electricity flows from the

¹ Jour. Iron and Steel Inst., 1, 70 (1909).

metal to the solution at the point where the metal passes into solution, through the solution to the metal at the point where the ions of the second metal are plating out, and back through the first metal to the starting-point again. The electrolytic double layers are thus destroyed, an electric current passes, and the solvent action of the water on the first metal continues.

"This phenomenon and its relation to the corrosion of iron are clearly exemplified in the well-known Daniel or gravity cell. In the case of pure iron in water a perfectly analogous condition is found to exist. Water itself is dissociated to a small but perfectly definite extent into its ions, hydrogen (H) and hydroxyl (OH). When a strip of pure iron comes into contact with water, it sends into the water iron atoms in the form of positively charged ions. Hydrogen as a metal has a much smaller solution pressure than iron, and hence an equivalent number of hydrogen ions plate out on the iron strip (leaving the free hydroxyl ions with their negative charges to balance the iron ions with their positive charges), and an electric current flows from the iron by means of the iron ions to the solution, and by means of the hydrogens from the solution back to the iron again, thus completing the circuit. But here comes an important break in the analogy of the film of copper in the Daniel cell. Deposited copper is a good conductor of the current, and offers no resistance to its flow from the solution to the iron on which it is attached. The reverse is true of the deposited hydrogen; here we have a high insulator — a film of gas which offers a great resistance to the flow of the current. Hence, although in the case of the iron strip in water all the conditions for continuous solution are present, owing to the resistance offered by the deposited hydrogen film (called polarization) the action must cease.

"Just as in the case of iron in a copper sulphate solution, the rapidity of the action depended upon the number of copper ions present in the solution, so here the solution of the iron, in the first instance, depends upon the number of the hydrogen ions present. This number of hydrogen ions, or the concentration of these ions, is increased by the addition of any acid. So weak an acid as carbonic increases the number, but to a relatively small amount; while a strong acid, like hydrochloric or sulphuric, adds to the number to such an extent that the solvent action becomes violent, and the deposited hydrogen comes off as a stream of gas.

"Since the presence of the polarizing film of hydrogen arrests the further solution of the iron, it is obvious that in order for the reaction to proceed this hydrogen must be removed. The destruction of the hydrogen film in ordinary corrosion is accomplished by the oxygen of the atmosphere, which is dissolved in the water. The action here taking place is a simple union of the hydrogen on the iron and the oxygen dissolved from the air, with the re-formation of water. It follows from this that any substance which dissolves or reacts with hydrogen should accelerate corrosion. This is found to be in fact the case."

Development and Use of Ferroxyl Reagent. — It is a matter of common observation that iron usually corrodes rapidly at certain weak points, the effect produced being known as pitting. That this effect can best be explained by the electrolytic theory there can be no doubt, and it was in the effort to obtain an actual demonstration that the now well-known "ferroxyl" reagent was evolved.¹ Early in his investigations one of the authors observed that whenever a specimen of iron or steel is immersed in water or a dilute neutral solution of an electrolyte to which a sufficient quantity of phenolphthalein indicator has been added, a pink color is developed. If the solution is allowed to stand perfectly quiet, it will be noticed that the pink color is confined to certain spots or nodes on the surface. The pink color of the indicator is a proof of the presence of hydroxyl ions, and thus indicates the negative poles. It may be added that some specimens of steel exhibit this phenomenon much more quickly and distinctly than others.

Since phenolphthalein shows only the nodes where solution of iron and subsequent oxidation does not take place, Walker² suggested the addition of a trace of potassium ferricyanide to the reacting solution, in order to furnish an indicator for the ferrous ions whose appearance marks the positive poles. If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound. Walker further showed that if the reagent is stiffened with gelatin or agar-agar, diffusion is prevented and the effects produced are preserved. For this combined reagent, which indicates at one and the same time the appearance of hydroxyl and ferrous ions at opposite

¹ Announced in a paper before the American Soc. Testing Materials, June 21, 1907.

² Jour. Am. Chem. Soc., 29, 1257, October, 1907.

poles, one of the authors has suggested for the sake of brevity the name "ferroxyl." If the reagent has been properly prepared, the color effects are strong and beautiful. In the course of a few days the maximum degree of beauty in the colors is obtained, after which a gradual deterioration sets in, although the effects can be preserved for a long time by flooding the jelly with alcohol.

In the pink zones, as would naturally be expected, the iron remains quite bright as long as the pink color persists. In the blue zones the iron passes into solution and continually oxidizes, with a resulting formation of rust. Even the purest iron develops the nodes in the ferroxyl indicator, but impure and badly segregated metal develops the colors with greater rapidity and with bolder outlines. This result would of course be expected, as in pure iron the formation of poles would be conditioned by a much more delicate equilibrium than in impure iron, where variations in concentration of the dissolved impurities would stimulate the electrolytic effects. Even so-called chemically pure iron contains small quantities of dissolved gases, and it is not improbable that even slight variations in the physical homogeneity of pure iron will occasion the electrolytic effects which are made visible by this delicate reagent.

Ferroxyl Indicator shows that Solution Tension of Iron Varies at Different Points on the Surface.—It should be remembered that the electrolytic action indicated by the ferroxyl tests is conditioned by a very delicate equilibrium. In order to decompose water by the electric current a very much higher difference of potential is needed than ever exists between points on the surface of a piece of corroding iron or steel, however badly segregated it may be. The entire value of the ferroxyl test consists in the fact that it indicates in a very delicate way that the solution tension of iron is higher at certain points on the surface than it is at others. Or, in other words, that certain surface points are, be it ever so slightly, electro-positive to others.

The very delicacy of the test shows that it must be carried out with precise care. If a sewing needle is taken and rubbed with the finger at one end and then placed in the reagent and left there, it will be noticed that where the fingers had come in contact with the steel, the slight trace of sodium chloride from the fingers will cause corrosion to commence and continue.¹

¹ See Stead, Jour. Iron and Steel Inst., 1, 97 (1909).

Bresch¹ in a short review of the new theory of corrosion has made use of a graphic method to show the action which takes place when a piece of iron is immersed in the ferroxyl reagent. This diagram, which is self-explanatory, is shown in Fig. 8.

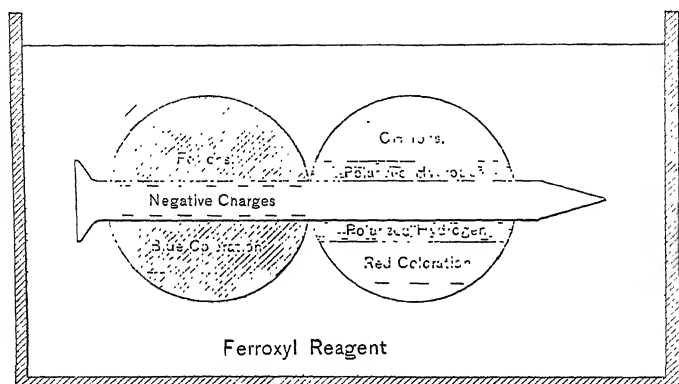


FIG. 8.—Diagrammatic explanation of action in ferroxyl indicator.

Preparation of Ferroxyl Mounts.—The ferroxyl mounts are prepared as follows: A 1½ per cent. solution of agar-agar is first made by dissolving a weighed quantity of powdered agar in the requisite amount of water. This solution is boiled for one hour, fresh water being added to replace that lost by evaporation. It is then filtered while hot and 2 c.c. of standard phenolphthalein indicator added to every 100 c.c. solution, after which it is brought to a perfectly neutral condition by titration with a tenth-normal solution of potassium hydroxide (KOH) or hydrochloric acid (HCl), as the case may be. The addition of 7 c.c. of a 1 per cent. solution of potassium ferricyanide to every 100 c.c. of solution is then made, and the ferroxyl reagent, while still hot, is ready to use. Enough of the reagent should be poured into a Petri dish to just cover the bottom, and the dish floated in cold water until the agar has jellied. A clean sample of iron is then placed on this bed of jelly and covered with the hot solution. After the final addition of agar the dish should not be moved until thoroughly cool. While the colors sometimes show up immediately, they usually require from twelve to twenty-four hours to attain their most perfect development. The mounts may be preserved for many months by keeping the surface of the agar covered with alcohol.

¹La Nature, Nov. 13, 1909, p. 373.

Ferroxyl Indicator Rational Proof of Electrolytic Theory. — These effects which are produced in the ferroxyl indicator constitute a visible demonstration of electrolytic action taking place on the surface of iron and causing rapid corrosion at the positive nodes.

The ferroxyl test in the hands of a number of investigators has brought out with clearness a considerable body of evidence to show that the electrolytic theory is in accord with observed facts when iron is undergoing corrosion. Some of the best results obtained are shown in Figs. 9, 10, 11, 12, and 13.

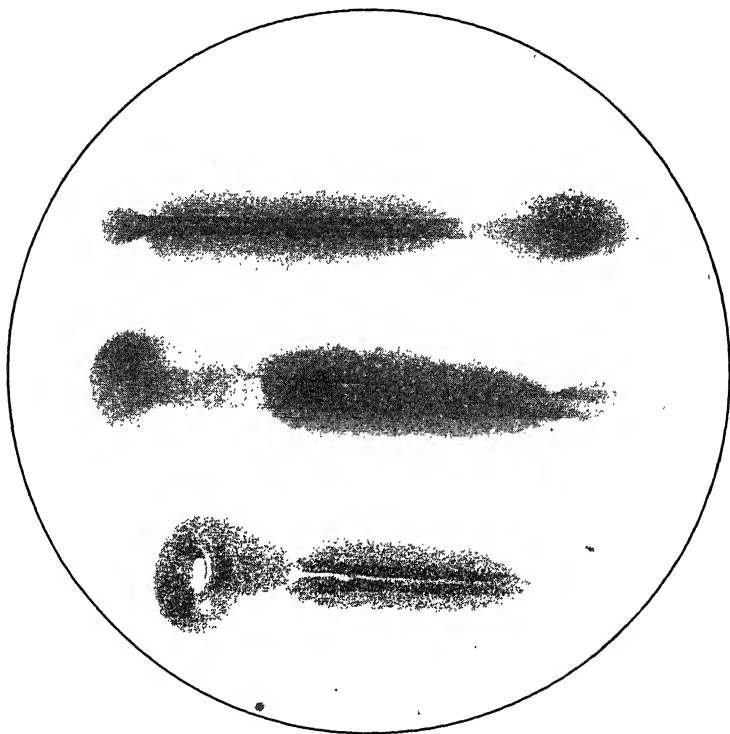


FIG. 9. — Showing some results obtained in the ferroxyl test. (Cushman.)

Varied Rust Formation in Different Samples. — It has been noted by a number of investigators that different samples of iron and steel do not rust in the same way when subjected to the action of water and air. While some samples show localized

electrolytic action, as indicated by deep pitting, others become covered with a more or less homogeneous coating of hydroxide, which shows little or no tendency to localize in spots or nodes. The question naturally arises: In what respect do these two

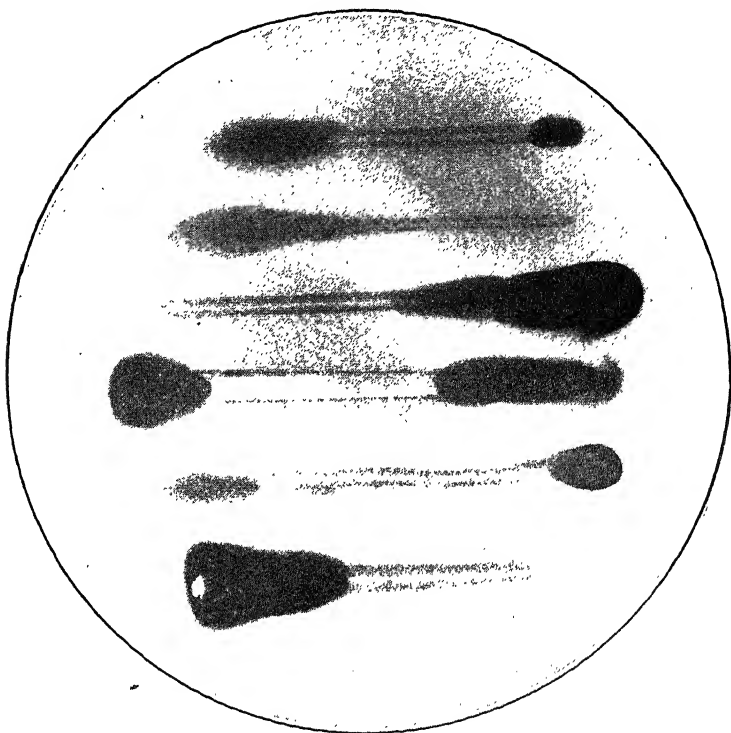


FIG. 10. — Showing a number of iron and steel objects immersed in the ferroxyl jelly. (Cushman.)

methods of rust formation differ? A close inspection of Fig. 13 is suggestive if not conclusive of the answer in this respect. The photographic reproduction exhibits an effect which is frequently observed in the ferroxyl tests. When the colors first developed, two dark blue nodes formed at the opposite ends of the test piece,

with a large pink area in the center, where for a time the metal remained quite bright. Very shortly, however, the poles changed, and the pink central area disappeared and gave way to a large blue node which enveloped three-quarters of the test piece, with

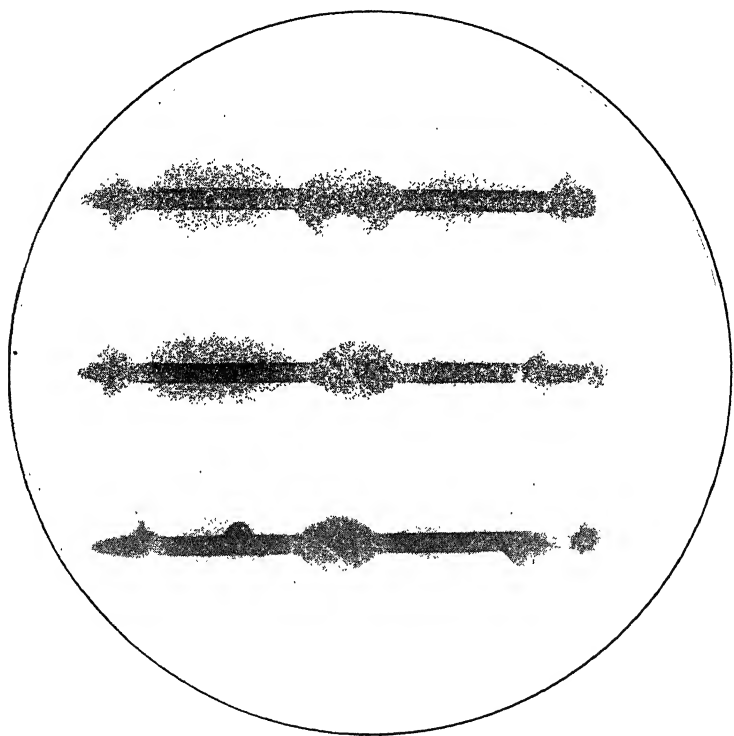


FIG. 11.—Steel wire nails in ferroxyl jelly. (Cushman.)

a small opposed pinkish spot. Again and again a reversal and change of poles took place, and at least five such changes are clearly shown in Fig. 13. As a result of this action the metal strip was rapidly covered over its entire surface with the same superficial, loosely adherent coating of hydroxide, which is

obtained in many cases when certain samples of iron and steel are allowed to rust under a layer of water. It is presumable that as the surface of the metal is eaten into by the solution of the iron at the positive poles, a new condition of equilibrium occurs,

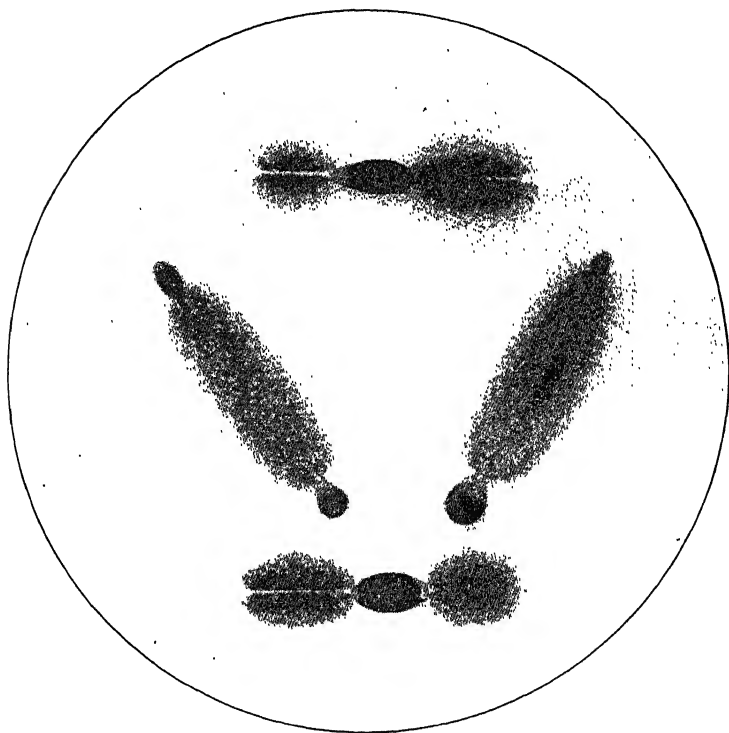


FIG. 12.—Steel nails in ferroxyl reagent. (Walker.)

resulting in changes and even reversals of the positive and negative nodes. This would indicate that in the case of metals which suffer from local action or pitting the segregation conditions are of a different nature from those which exist in the case of metals which rust more evenly. A rough analogy may be drawn by

imagining an imperfect mixture of black and white sand, the respective grains of which may lie in streaks, spots, and layers, or may tend to arrange themselves in some more or less uniform relation to each other. The best demonstration that the rusting

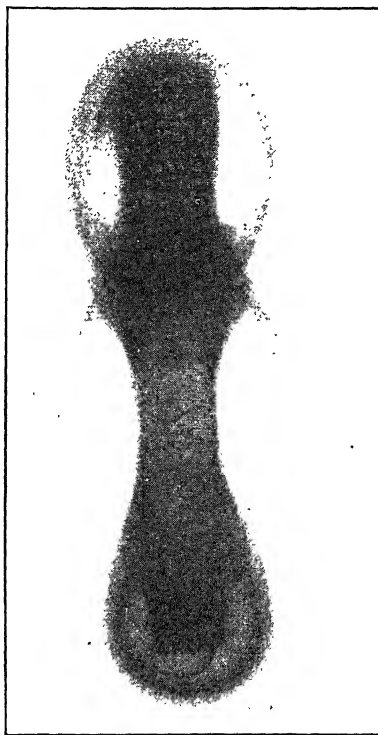


FIG. 13. — Strip of steel in ferroxyl reagent, showing frequent shifting of (Cushman.)

and corrosion of iron and steel in all its forms is essentially an electrolytic phenomenon is afforded by the fact that it has not as yet been possible to find a specimen of such purity that no trace of positive and negative nodes will be formed in the ferroxyl indicator.

CHAPTER IV

APPLICATION OF ELECTROLYTIC THEORY

Two Distinct Effects in Rust Formation. — We may now apply the electrolytic theory to the actual results obtained in the ordinary rusting of iron. If a section of rolled metal, such as sheet or plate, is immersed in water, according to the electrolytic theory, rusting must take place with the establishment of positive and negative spots or areas. At the positive points iron will pass into solution and be rapidly oxidized to the loose colloidal form of ferric hydroxide which is characteristic of rust formed under these conditions. It is a well-known fact that colloidal ferric hydroxide will move or migrate to the negative pole if subjected to electrolysis.¹ We may therefore consider the possibility of two separate effects that may be produced, viz., when a positive center is surrounded by a negative area, and vice versa. These two conditions may be graphically represented by the two circles A and B shown in Fig. 14.

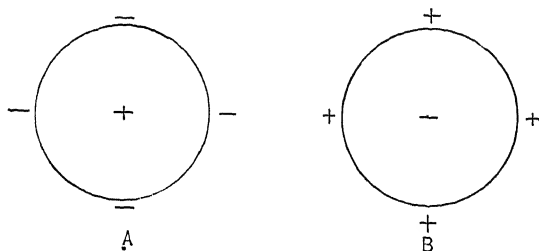


FIG. 14. — Diagram illustrating the electrolytic action on the surfaces of iron and steel.

Now, as rusting proceeds we should expect in the case of A that the ferric hydroxide would be piled up in a crater formation, while the metal is eaten out at the center. In the case of B the effect would be reversed, and while the metal would be attacked in the surrounding area the hydroxide would be piled up in a

¹ See page 33.

cone at the center. That this is precisely what is taking place whenever a sheet of metal rusts under water a low-power microscope very clearly shows. In Figs. 15, 16, 17, and 18 the writer has succeeded in showing the existence of both the craters and cones as they formed on the surface of a piece of wrought-iron boiler plate. In Fig. 15 a typical crater surrounding the point of pitting is shown, while in Fig. 16 an excellent example of the

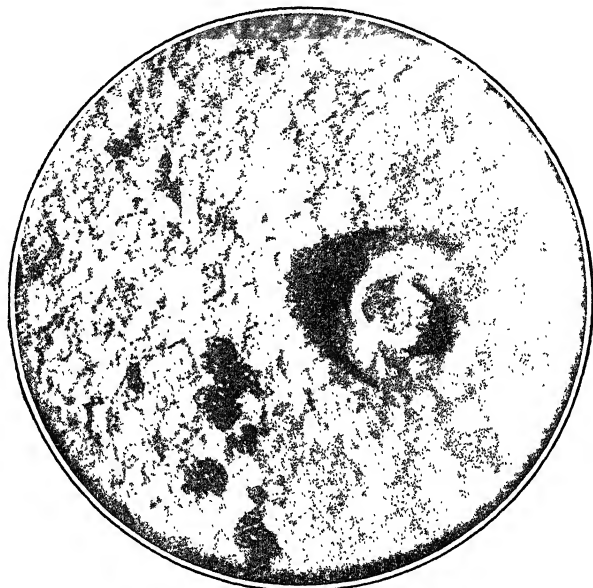


FIG. 15. — Formation of crater with pitting effect in center. (Enlarged 45 diameters.)

cone appears. Both are photomicrographs magnified about 45 diameters. The source of light was on the right in each case, and the shadows indicate the crater and cone formation, which is so clearly discernible under the microscope. Figs. 17 and 18 are from photographs of the rusted metal, showing the craters and cones as they appeared with very low magnification.

Fig. 19 shows the surfaces of strips of Bessemer steel (s), puddled wrought iron (z), and charcoal iron (c), prepared in the following manner: The respective samples were turned off in a lathe to a bright, smooth finish; they were then immersed under a thin layer of the ferroxyl reagent and allowed to stand quietly

for several days. At the end of this time the surfaces were wiped clean. The electrolytic effects, which had been active on all three metals, are very well illustrated. The light portions show the negative areas, where little or no rusting took place, while the dark spots and areas show the special points of attack, with the pitting effects. The etching is not, of course, deep in the

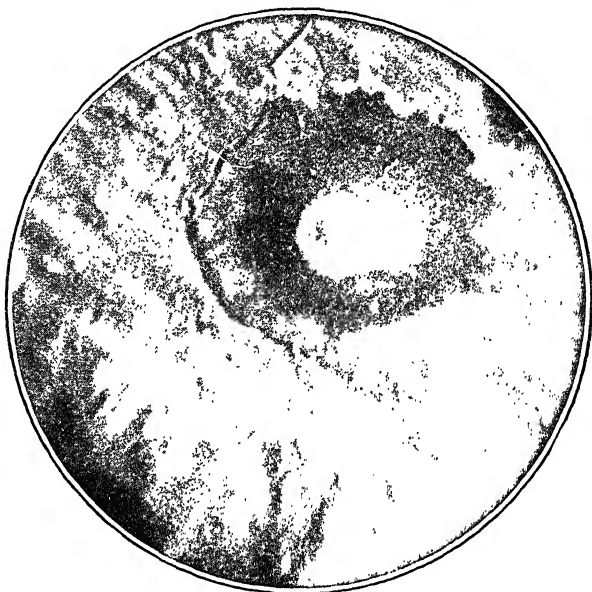


FIG. 16. — Formation of cone with pitting effect in surrounding area. (Enlarged 45 diameters.)

case of any of the three samples, and should not be understood as showing the relative rate of corrosion of the different types of metal. The specimens simply serve as a demonstration that the rusting in each case has been accompanied by electrolysis.

In Fig. 20 is shown a photograph of the actual pitting of a boiler tube, which failed, after eighteen months' service, in a water-tube type of marine boiler. The conclusion that pitting was due to electrolysis seems justified by comparing this photograph with those shown in Figs. 17 and 18.

Practical Application of Electrolytic Theory. — The evidence advanced in the preceding pages appears to the writers to confirm the conclusion that the whole subject of the corrosion of iron is

an electro-chemical one, which can be readily explained under the modern theory of solutions. It is an undeniable fact that some irons and steels suffer corrosion very much more rapidly than others, and the underlying causes for these differences constitute one of the important problems of modern metallurgy.

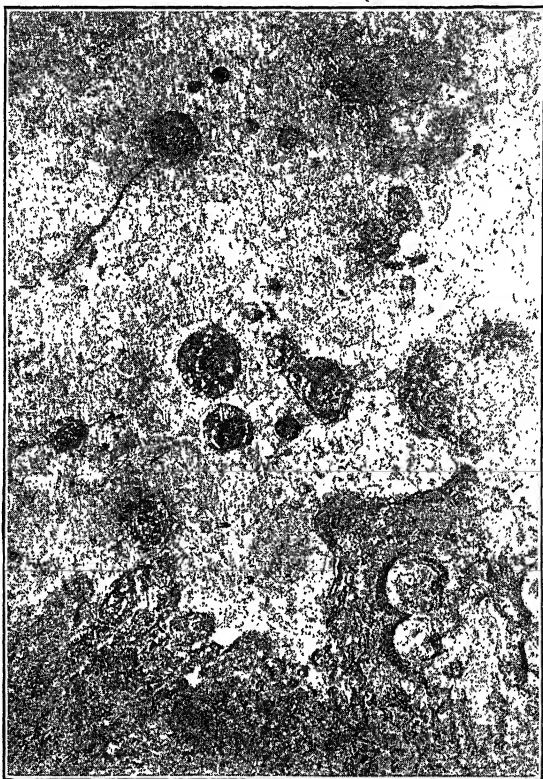


FIG. 17. — Photographic representation of rust-spots formed on the surface of iron.

Although the discussions brought forward up to this point are mainly theoretical in their nature, it is quite apparent that they also have an indirect practical bearing. Before advance can be made in overcoming the difficulties in the way of manufacturing iron which shall have the maximum resistance to corrosion, as well as the preservation of the metal under the conditions of service, the underlying causes must be thoroughly

understood. If we accept the electro-chemical explanation of the corrosion of iron, there can be no doubt that conditions which inhibit electrolytic effects also inhibit corrosion, and vice versa. The purer the iron in respect to certain other metals which differ electro-chemically from iron, and the more carefully lack of homogeneity and bad segregation are guarded against, the less



FIG. 18. —Photographic representation of rust-spots formed on the surface of iron.

likely are the electrolytic effects to become serious. These points constitute the essential problems which confront the manufacturer who desires to make a product which shall have a high resistance to corrosion. The user and consumer, however, are interested in the protection of the various types of merchantable iron and steel which are available under market conditions at

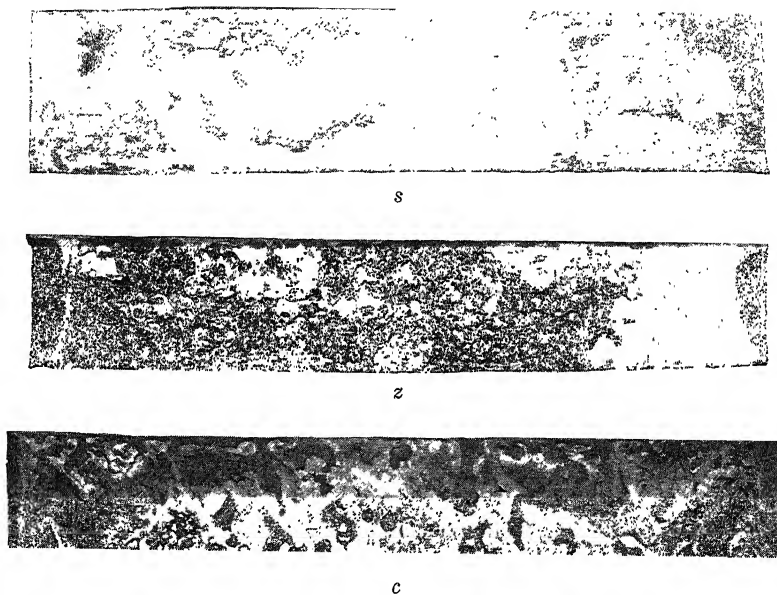


FIG. 19. — Strips of Bessemer steel (*s*), puddled wrought iron (*z*), and charcoal iron (*c*) after immersion in ferroxyl indicator.

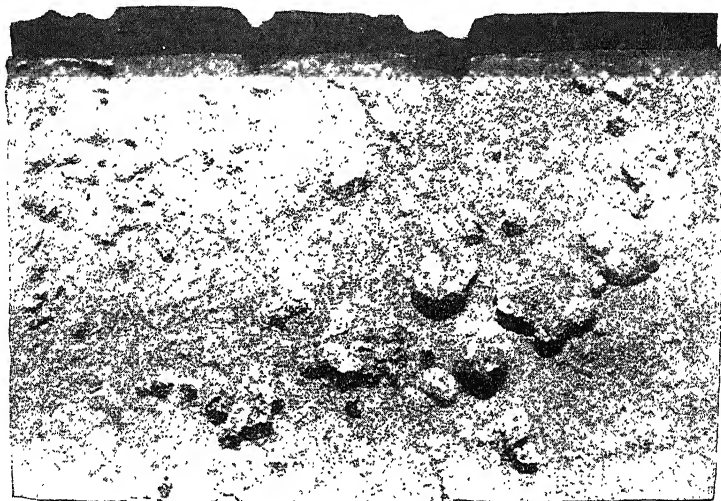


FIG. 20. — Actual pitting of tube in water-tube type of marine boiler.

the present time. In short, protective coatings and palliative methods of treatment are in greater demand to-day than ever before. From the standpoint of the electrolytic theory many suggestions for experiment under the conditions of service present themselves.

Walker has used the ferroxyl indicator to illustrate the application of the electrolytic theory to practical problems. This author states:¹

"When a piece of iron is placed in ordinary water, exposed to the air, it will dissolve or rust. If now there be placed in the water with this piece of iron a piece of platinum, the solvent or corroding action of the water will not be changed. The oxygen is present in the solution as before, and the iron ions as they separate from the metallic iron are being oxidized and precipitated as rust. If now the platinum and iron be electrically connected, a marked increase in the rate of the solution or corrosion of the iron is noticed. No chemical condition has been changed; the difference lies in the fact that there is now an electrical contact between the iron and the platinum, and the platinum furnishes a surface on which the hydrogen can deposit, and on which, by virtue of its catalysing action, the hydrogen will be rapidly oxidized by the dissolved oxygen, and thus removed from the sphere of action. This is shown in Fig. 21. A piece of platinum wire is seen in the center of the plate. A nail is also seen corroding at the ends and setting free hydrogen in the center. A second nail is connected with a platinum wire. The red of the phenolphthalein is seen around this wire, while the nail is corroding very much faster than the unconnected nail.

"Another example is found in the action of zinc in water containing an electrolyte. If a strip of zinc and a piece of iron be placed in water containing a very little salt, the iron will corrode rapidly, while the zinc will be but slightly attacked. The usual explanation for this phenomenon is that the zinc protects itself with an adherent film of zinc oxide or hydroxide, while the iron produces a non-adherent voluminous hydroxide, which does not protect. If now instead of being separated the two strips of metal be placed so as to touch each other, the iron no longer corrodes, but the zinc very rapidly passes into solution. This action is shown in Fig. 22. A piece of zinc is seen at the center,

¹ Jour. Iron and Steel Inst., 1909, I.

corroding slightly from the ends, and showing the red due to the separating hydrogen ions at the center. Zinc ferricyanide is white, and hence the same reagent demonstrates the separation of zinc ions just as it does the iron ions in the plates already considered, in which the positive poles are shown in blue. The nail which has been connected to another piece of zinc is not corroding, but is protected by the separating hydrogen. The zinc thus connected, however, is seen to be rapidly dissolving."

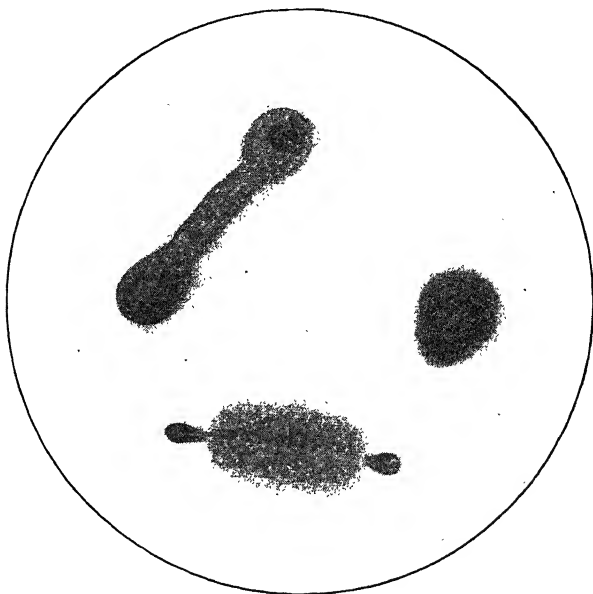


FIG. 21. — A piece of platinum wire is seen in the center of the plate. Shows the action of the electro-negative metal, platinum, stimulating the corrosion of iron. (Walker.)

This point which is so beautifully illustrated here has a most interesting bearing on the galvanizing problem. It will at once be seen that the zinc coating which is applied to steel in the galvanizing processes has a double function to fulfil. In the first place it is designed to keep the surface of the steel from coming into contact with water and the atmosphere, and secondly it enacts the heroic role of self-sacrifice to the protection of the iron whenever water and oxygen finally succeed in breaking

through. The practical applications of this theoretical treatment of the subject must await detailed presentation in a succeeding chapter.

Walker's next demonstration, as illustrated in Fig. 23, shows the opposite tendency at work. In this case a piece of mill-scale is shown in the center, and in addition to this the effect produced



FIG. 22. — A piece of zinc is shown in the center. Shows the protective action of the electro-positive metal, zinc, on the corrosion of iron. (Walker.)

by connecting a fragment of mill-scale to a piece of steel. The mill-scale, which consists of the magnetic oxide of iron, is electro-negative to the iron, and is therefore acting a part directly opposite to that of the zinc in the preceding illustration. That is to say, instead of retarding the corrosion of the iron at its own expense, it is stimulating the attack made upon it by the electrolyte.

These as well as many other observations and experiments, based upon the electrolytic theory, have a direct bearing upon many of the practical problems met with in the manufacture and use of iron and steel. These problems, as they affect the resistance to corrosion, will be discussed in the following order:

- (1) Effect of purity and chemical constitution of the metal.
- (2) Effect of heat treatment, annealing, tempering, condition of surface, etc.
- (3) Effect of state of purity of the rusting medium, electrolytes, natural water, the atmosphere.



FIG. 23. — A piece of mill scale is shown in the center. Shows the stimulated corrosion of iron affected by contact with the electro-negative magnetic oxide of iron. (Walker.)

Modern Steels seem more Corrodible than the Old. — A mass of evidence appears to show that the old slowly fabricated irons of thirty years ago are much more resistant to corrosion than modern steels. Sang, in summing up from the opinions of a number of authorities, discusses this phase of the subject as follows:¹

“From a theoretical standpoint, steel, being negative to iron, should be the least corrodible of the two. As a general thing, results of tests between iron and steel have, in the past, resulted in favor of the iron; in most cases, the experimenters were undoubtedly looking for the defeat of the new material, steel, and their state of mind helped them to find it. There are, however,

¹ Proc. Eng. Soc. West. Pa., XXIV, 10, p. 514.

a large and ever-increasing number of contrary observations recorded, especially where the tests have been carried out on a large commercial scale, and with qualities of recent manufacture. The opinion one is led to form from a careful examination of recorded observations is in agreement with that of Ewing Matheson,¹ namely, that properly protected steel and iron rust to about the same extent, the steel doing so more uniformly; this is, of course, subject to the variations of structure already referred to, and those of chemical composition, especially as regards metallic impurities, which will be considered later.

"A most important paper was presented before the Institute of Civil Engineers in 1881 by David Phillips,² 'On the comparative endurance of iron and mild steel when exposed to corrosive influences'; excellent tables are given, and the general conclusions favor iron. A distinction must here be made between the cast and wrought metal; cast iron will not rust as readily as wrought iron, unless the skin is removed, in which case it will rust faster.

"It must be borne in mind, as a limitation to all results ad-duced, that while the initial rusting may be greater with either material, iron or steel, the rates of progression may be different and may bring about a complete reversal in the final result; in material which rusted faster at first may outlive the other. This is especially apt to be the case with forged, rolled, and drawn metals. Future tests should, therefore, either be carried out to destruction, as advocated by Howe, or else to the point at which failure of the material in service would result from loss of useful area." Again in another paragraph Sang³ very truly says:

"Carelessness of manufacture, which tends to heterogeneousness, is an invitation to corrosion, and in itself goes far to explain why modern steel, which is tortured into shape at such a high speed that the molecules are not permitted to readjust themselves, is said to be more corrodible than the metals produced a generation ago; in those days iron and steel were produced in small quantities, without the addition of other metals, and were rolled slowly and allowed to cool naturally. The internal strains due to mechanical treatment are not to be confounded with the

¹ Proc. Inst. C. E., Vol. 69 (1882), p. 1.

² Proc. Inst. C. E., Vol. 65 (1881), p. 73.

³ Proc. Eng. Soc. West. Pa., XXIV, 10, p. 511.

unevennesses in the distribution of the impurities due to segregation in cooling; these mechanically induced strains are really equivalent to straining the metal beyond the elastic limit, which, as will be seen later, makes it more corrodible. Moreover, the tonnage-craze, from which the quality of product in so many industries is to-day suffering, is causing to be placed on the market a great mass of material, only a small proportion of which is properly inspected, which is not in proper condition to do its work — rails and axles which fail in service and steel skeletons for high buidlings which may carry in them the germs of destruction and death.”

Chemical Purity an Aid in Resisting Corrosion. — While wishing to avoid taking sides in the more or less heated controversy that has gone on for many years between the advocates of different types of metal, the authors are of the opinion that, other things being equal, the approach to chemical purity, whether the metal is classed as iron or steel, should lead to added resistance to corrosion. Indeed, it is impossible to accept the electrolytic theory without reaching this conclusion, for it follows naturally that the presence of impurities invites segregation in the structure of the metal with inevitable surface differences of potential and stimulated electrolytic action. All authorities who accept the electrolytic theory agree on this point. Walker says on this subject:

“Since before the iron can form rust it must first pass into solution, and in so doing cause an electric current to flow from the iron at that point to the iron at some other point, any circumstance which will aid the flow of this current will accelerate the solution of the iron. In other words, any differences in potential which may exist upon the surface of the iron will in itself cause a flow of electricity which will result in a solvent action on the iron. Such differences of potential inevitably result from a segregation or uneven distribution of any impurities which the iron or steel may contain. Hence we should expect that the speed of corrosion would increase in accordance with the percentage of impurities present, and it should decrease in accordance with the care bestowed upon the iron or steel during its manufacture to prevent a segregation of these impurities. The simplest way, of course, to insure an absence of segregation is to eliminate altogether those materials not needed in the iron. It

has been found that a steel made under such conditions that the total impurities are reduced to not over five hundredths of 1 per cent. (0.05 per cent.) resists corrosion to an extent equal to the iron of our forefathers. The steel companies have been slow to accept this general proposition, but it is gratifying to know that material of this purity may now be obtained on the open market."

Difficulties Introduced by Improper Heat Treatment, etc. — To sum up this phase of the subject we may say that, *other things being equal*, the electrolytic theory points to the fact that the purer and least segregated metals should be most resistant to corrosion. At the same time it should not be forgotten that it is always possible to leave the frying-pan for the fire, and that in the effort to arrive at chemical purity in the processes of manufacture the metal may have come to harm by burning, gas occlusion, or faulty heat treatment. It is also true that in the effort to reach chemical purity the physical characteristics may be changed, to the damage of the metal produced. Unfortunately, analysts do not as a rule consider the question of occluded gas, and yet this factor undoubtedly has much to do with resistance to corrosion. Sang¹ has collected a mass of information from the literature of the subject bearing on this point. This author says, "Occluded gases must next claim attention. Graham found that iron cooled in hydrogen absorbed 46 per cent. of its volume. John Perry in 1872² detected the presence of hydrogen in steel. Ledebur found 0.0017 per cent. of hydrogen in a soft open-hearth steel. These observations are of interest because, hydrogen being negative to iron, it will, as already stated, promote its solution and corrosion. The electrolytic activity of hydrogen was pointed out by Roberts-Austen."³

"According to Lenz, 45 per cent. of the absorbed gases in iron may be hydrogen, the balance being carbonic dioxide, carbonic oxide, and nitrogen in about equal proportions. According to F. C. G. Muller,⁴ about 67.8 to 90.3 per cent. of the gas in steel is purely hydrogen.

"It is a well-known fact that iron or steel containing occluded hydrogen, due to pickling in acids, is hardened to a considerable

¹ Proc. Eng. Soc. West. Pa., XXIV, 10, p. 504.

² Jour. Iron and Steel Inst., Yr. 1872, p. 240.

³ Fifth Report, Alloys Research Comm., Inst. Mech. Engrs., 1889.

⁴ Deuts. Chem. Gesell., Vol. XII (1878), p. 11.

extent, and is readily oxidized while in that condition; thorough washing and neutralizing of the acid will not correct the hardness nor the readiness to oxidize. Gas occlusion by this method may, normally, reach 12 times the volume of the iron, proving that most of it must be alloyed or in a liquid or solid state. The greater proportion of this absorbed gas is hydrogen, and it must, necessarily, be as impure as that which rises in the pickling vats, containing, therefore, hydrogen sulphide, arsenide, etc.

"On the other hand, electrolytically produced iron, which is quite difficult to corrode, is hardened to a considerable extent by the absorption of hydrogen during its deposition. The hardness of electrolytic iron is 5.5 as against 4.5 for ordinary iron. According to Cailletet,¹ electrolytic iron will hold as much as 250 times its own volume of hydrogen, and the alloy containing 0.028 per cent. (by weight) of hydrogen will scratch glass. This absorbed hydrogen must be relatively pure, and while this may preclude electro-chemical activity among the gases themselves, it can hardly have much bearing on the difference of behavior between it and pickled iron, when exposed to corroding agencies.

"The hydrogen contained in pickled iron can be almost entirely baked out of it at a low temperature; not so with the hydrogen absorbed electrolytically. This tends to show that in the pickled iron the gas is not so permanently or stably combined — if combined at all — as in electrolytic iron. Furthermore, the great volume of the gas taken in by the electrolytic iron shows that a very large percentage must exist in solution as an alloy with the iron. The coexistence of three states of matter has been supported by Graham, Wiedermann, and Spring. While there may be just as much free dissociated hydrogen contained in the pores of both classes of iron, and the tendency to rust from that cause may be the same, yet the larger amount of hydrogen-iron alloy in the electrolytic iron may resist corrosion much better than iron alone. The quality of resistivity to corrosion is intimately connected with the rise in electrical conductivity which is brought about by the chemical union of hydrogen with metals. Hot iron when quenched in water absorbs hydrogen, and Richards and Behr² have found that the electrode potential was raised by 0.15 volt, the nature of the gas being apparently the same as that

¹ C. R., Vol. LXXX (1875), p. 319.

² T. W. Richards & G. E. Behr Jr., *Zeits. Phys. Chem.*, March 5, 1907.

which is absorbed in the presence of nascent hydrogen, and therefore by electrolysis. The hydrogen taken up by finely powdered iron reduced at a low temperature was not found to affect the e.m.f.; we may infer that the physical conditions attending the production of this iron were insufficiently powerful to cause the alloying on which the change of e.m.f. seems to depend. Dr. Steinmetz finds that electrolytic iron has a very high hysteresis loss, but attributes it to occluded nitrogen.¹

"From an examination of all these facts, it would appear that the increase of potential due to the alloyed hydrogen in electrolytic iron overcomes the effect, as an electro-negative catalyzer or otherwise, of hydrogen in a free ionic state only. In all classes of iron the hydrogen exists in both conditions, free and combined, just as carbon does in pig iron, but the proportion of hydrogen-iron alloy in electrolytic iron is very much greater than in the other metals. Hydrogen, like carbon, when present in a free state will by contact action promote corrosion; like carbon also, when chemically combined with the iron it will resist corrosion, but if the alloy is unevenly distributed the pure iron in contact with the alloy will be attacked.

"According to Roberts-Austen, silicon, manganese, and aluminium prevent the escape of hydrogen from iron; Ledebur claims,² however, that brittleness after pickling, due to hydrogen, is greater if the combined carbon is high, while silicon has the reverse effect; he is in accord, therefore, with Troost and Hautefeuille,³ who claim that silicon diminishes absorption. These seemingly opposite statements may be reconciled by assuming that while silicon may reduce the absorption of hydrogen, it will also retard its subsequent removal, just as non-conductors which absorb heat with great difficulty will, on that very account, retain it the easier. Manganese is said ⁴ to greatly increase the absorption of the gas while diminishing that of carbonic oxide, which is, in any case, very slight. Manganiferous pig iron retains more gas than does ordinary pig.

¹ For a discussion of the important influence of nitrogen on the physical characteristics of steel, see Giesen, *The Special Steels in Theory and Practice*, Carnegie Scholarship Memoirs, Iron and Steel Institute, I (1909). See also Stromeyer, *Jour. Iron and Steel Inst.*, I (1909).

² *Mitt. Kon. Tech. Versuchsanstalten, Ber. Yr. 1890. Suppl., I, 1907.*

³ *An. Ch. & Ph., 5e S., Vol. VII, p. 1155.*

⁴ *An. Ch. & Ph., 5e S., Vol. VIII, p. 1155.*

"Pressure applied during the solidification of metals — as, for instance, in the Whitworth process — prevents the escape of the gases. They can be driven out by heating, preferably *in vacuo*, or locally by machining or drilling; the combination is, therefore, not a very close one. To drive the gases out of pig iron, a temperature of 800° C. is sufficient. Malleable iron contains more carbonic oxide than hydrogen, and it is retained with greater energy. Steel is said to absorb somewhat less than cast iron, and wrought iron less than cast iron; these differences are, in great measure, no doubt, functions of the porosity.

"Occluded gases, and especially hydrogen, must not be lost sight of when dealing with the problem of corrosion. Hydrogen is the lightest, and, therefore, kinetically the most active of elements; it is, in a way, a sort of universal catalyzing 'dæmon,' an extravagant statement to the ear, perhaps, but with some merit of suggestiveness; all chemical reactions take place in the presence of hydrogen, and it is the only element of which this is true. Hydrogen, which seems to form the main ejection from the sun, and may be regarded as closest to the primordial element from which, according to recent well-grounded theories, all other elements may proceed, is unique in many of its properties; it seems to stand apart from the other elements in many ways. These differences are, in many cases, attributable to the great activity of its molecules in proportion to their mass, hence, for instance, the distinct character of its curve representing the value of p_v under different pressures.

"The diffusion through a finely porous material, which gives rise to dissociation, is similar to, if not identical with, osmosis; in osmosis the porous membrane causes dissociation resulting in chemical effects which are the basis of important reactions, and, among others, of organic growth and life.

"Hydrogen will pass through platinum and red-hot iron. (Ste. Claire-Deville) and its ready dissociation, which was demonstrated in Winklemann's important study of its diffusion through palladium,¹ suggests a belief in its breakdown, under conditions of common occurrence, into free and active atoms, ready to take the first opportunity offered of entering into a combination. The condition of most common occurrence is, as we have seen, the contact of dissimilar substances. The occlusion of free hydrogen

¹ An. Phys. Chem. Wied., Vol. 6, p. 104, and Vol. 8, p. 388.

in coal-dust, wheat-dust, zinc-dust, and other dusts, will go far to account for their detonation by spontaneous oxidation. These dusts act in the same way as does spongy platinum on certain gases which it ignites by simple contact. A porous material like iron or steel should have a similar effect, but its action would be slow and progressive instead of sudden; instead of spontaneous oxidation we get slow oxidation, rusting.

"We thus have additional reason to believe that free dissociated hydrogen ions, generated by the electro-chemical action on moisture of iron in contact with its impurities or other substances exterior to itself, induces by catalytic excitation, or an electrical effect of its contact with the iron, the solution of that iron as free ferrous ions which unite with free oxygen to form rust."

It will be seen from the above citations that the occurrence of gases in steel is a matter of great importance which has not received the attention from manufacturers that it deserves. That the resistance to corrosion is influenced by occluded gases is highly probable. The authors are glad to take this occasion to recommend to manufacturers who are aiming at the production of pure irons, that this subject be given more careful study in the future. Baker¹ has recently published a valuable paper on gases occluded in steel, with an account of methods for estimating them.

The Carbon Constituents of Steel. — It is not the authors' intention to include in this work instruction in the metallography of steel. For full information on this subject the special works should be consulted. In view, however, of the possible influence of the carbon compounds in iron on the electrolytic effects which are observed, a brief reference to the general substance is here included. The microscopic examination of almost any steel when properly mounted and prepared will show that the structure is not by any means homogeneous, but that it contains recognizable constituents. Specimens of pure iron, when properly polished and etched, exhibit a peculiar coarse-grained structure under the microscope to which the name ferrite has been given. As the percentage of carbon rises in steel various peculiar and characteristic structures make their appearance, corresponding to certain definite compounds, solid solutions, and eutectics. It does not follow that all these structures are different substances, as they

¹ Iron and Steel Inst., Carnegie Scholarship Memoirs, Vol. I, 1909.

may be allotropic modifications or phases of one and the same substance. Carbon in steel does not exist in the free state, as it does in cast iron, but it combines with iron forming the carbide of iron, Fe_3C . This carbide appears as dark areas of peculiar and characteristic appearance to which the name cementite has been given, because it occurs abundantly in steel, treated by the cementation process. When examined under a high magnification carbon steels show patches that exhibit a pearly luster, owing to a finely lamellar structure. This constituent has been called pearlite, and is now known to consist of a banded structure of cementite and ferrite, in definite proportions, not being a compound, but simply an intimate mixture. There are a number of other constituents which correspond to different quantities and conditions of the combined carbon in hardened steel. To these such names as austenite, martensite, troostite, osmondite, and sorbite have been given in honor of eminent metallographists.

Austenite is produced by quenching high carbon steel in ice water from a temperature above 1050°C . It is not often met with, and is probably of little importance in any discussion on corrosive tendency.

Martensite is defined as the constituent that confers hardness on steel. It is characterized by a finely interlaced structure, and is found only in hardened steels.

In regard to troostite and sorbite little is known; they make their appearance when steel is subjected to definite quenching and tempering processes. Osmondite is a name which has recently been proposed to define a characteristic transition point that occurs in the tempering of quenched steels.¹

According to Campbell,² "Pearlite is an 'eutectic alloy,' a term which may possibly not be familiar to all readers. An eutectic alloy is formed by the simultaneous crystallization of different metals in a liquid mixture, as for example, a mixture of copper and silver. These metals form an alloy in the proportions of 72 per cent. silver and 28 per cent. copper at a temperature of 770°C . (1418°F .), and if a melted mixture of these two metals contain any different proportion than this, and if it be allowed to cool, the element in excess of this proportion crystallizes out, the crystals remaining uniformly distributed through-

¹ Heyn and Bauer, Jour. Iron and Steel Inst., 1, 112 (1909).

² Manufacture and Properties of Iron and Steel, Campbell, p. 298.

out the molten mass. When the critical point of 770° C. is reached, the alloy of 72 silver and 28 copper becomes solid, and entrains the innumerable crystals of the excess element which have separated from the mother liquid. A little consideration will show that under the microscope the element solidifying first and the eutectic alloy will occupy areas exactly proportional to the original constitution.

"In steel at high temperatures the same conditions exist as in the mass of silver and copper just described, save that the elements are in what is called 'solid solution,' martensite at the lowest critical point going through a transition into ferrite and cementite. The element in excess separates by itself, and when the proper relation has been established the ferrite and cementite crystallize together in most intimate mixture to form pearlite. As stated previously, the excess of cementite or ferrite begins to form by itself at the upper critical point, a small amount being found in steel quenched just below this, and at the second point this amount is increased, but this excess is always small except in the case of low carbon steel.

"The foregoing argument may be summarized as stated by Sauveur:

"(1) All unhardened steels are composed of pearlite alone, or of pearlite associated with ferrite or cementite.

"(2) Without taking into consideration austenite and troostite, hardened steel is composed of martensite alone, or of martensite associated with ferrite or cementite.

"(3) Ferrite and cementite cannot exist together in the same piece of steel.

"(4) The presence of the lamellar variety of pearlite is almost certain proof that the steel has been annealed.

"Following the proposition that ferrite is iron free from carbon, and that cementite is a compound represented by the formula, Fe_3C , it is evident that in very low steels, say ranging from .02 to .10 carbon, the structure will be almost entirely ferrite, and that in steel of 2.00 per cent. carbon there will be an excess of cementite. There will therefore be one point of carbon content at which the component ferrite and cementite will both be satisfied, which is to say that the original proportion will be that of the eutectic alloy. This occurs in a pure steel containing about .80 per cent. of carbon, the micro-structure of this grade showing no ferrite or cementite."

Influence of Iron-Carbon Constituents on Corrosion. — The influence of the quantity and condition of the contained carbon of a steel on the tendency to corrosion opens up a most interesting field of inquiry, in which unfortunately the information is meager, and to a considerable degree contradictory. A vast amount of theorizing has been done on this point alone, and the literature of the subject abounds with statements in regard to the influence of carbon which are certainly based on insufficient evidence. Howe believes in a mechanical protection afforded by carbon as rusting proceeds. This authority has stated:¹

“As steel is gradually corroded away, more and more of its surface should come to be composed of cementite, and this fact should tend to retard the corrosion of steel, because cementite should protect the underlying free iron or ferrite.”

And again: “The cementite is in such extremely minute microscopic plates that the eating away of a very small quantity of the iron from above them ought to bring very nearly the full proportion of this cementite to the surface.”

Sang claims that,² “Carbon, insomuch as it will allow hardening, will act as a protection, provided it is combined with the iron and uniformly distributed; high-carbon steel is less corrodible than mild steel or iron.”

There can be little doubt that maximum density in steel will contribute toward maximum resistance to corrosion provided segregation has not taken place, but in the authors' opinion it has not yet been proved that the majority of high-carbon steels in general use are less corrodible than mild steel or iron. This subject can, however, best be discussed under another heading, on the effect of heat treatment and tempering.

It is quite certain that more information is needed on the influence of carbon and the iron-carbon constituents on the corrosion problem. Munroe³ observed a number of years ago that in a case of corrosion of a cold-chisel with a soft shank and hardened cutting edge, the soft part was eaten away while the hardened edge had been protected. This observation has been many times confirmed until we may feel sure that in some cases soft iron (ferrite) is electro-positive to hardened steel (cementite) so

¹ Trans. Am. Soc. Testing Materials, 1906.

² Proc. Eng. Soc. West. Pa., XXIV, 10, p. 528.

³ Jour. Franklin Inst. 1883, 302.

that in contact in a corroding medium the latter will be protected at the expense of the former type. Sauveur states, as quoted above, that ferrite and cementite cannot exist together in the same piece of steel. This would seem to indicate that differences of potential in the same piece of steel would not be occasioned from this cause. Sauveur, of course, does not refer to the intimate mixture of ferrite and cementite known as pearlite, but in this case the structure is too definite and intimately mixed to lead to local electrolytic couples.

Possible Effect of Assembling Metals of Varying Carbon Types.—The association of steel and iron of different carbon content in structural work, is a question of the highest importance which has not received as much attention from engineers as it deserves. In this connection we may recur to the case already cited of the Diamond Shoal Light-vessel, in which in eleven years 8400 four-inch iron bolts were destroyed and had to be renewed.¹ In this and similar cases the more electro-positive metal is rapidly destroyed owing to the stimulated electrolysis, which is induced by the coupling of different types of metal.

Sang treats this subject as follows:² "Some tests were made in 1882 by J. Farquharson³ on six plates of iron and six of steel; these were immersed for six months in Portsmouth Harbor, six of each separately, the other six as connected couples; in this way the comparative corrosion of the iron and steel was obtained, and also the increase of corrosion due to galvanic action between steel and iron. The following table gives the losses observed in ounces and grains:

(a)	Steel } Iron }	in contact	{ 0-427 7-417
(b)	Steel } Iron }	separate	{ 3-340 3-327
(c)	Steel } Iron }	in contact	{ 0-297 7-770
(d)	Steel } Iron }	separate	{ 4-000 3-190
(e)	Steel } Iron }	in contact	{ 2-337 6-000

¹ See illustration (Fig. 4) and description p. 11.

² Proc. Eng. Soc. West. Pa., XXIV, 10, p. 520.

³ Trans. Inst. Nav. Arch., vol. 3 (1882), p. 143.

Steel } separate	{ 4-157
Iron }	{ 4-570

"These results, which were confirmed by Mr. W. Denny, from his experience in the case of the steamship *Ravenna*, are interesting to analyze. They show that in two cases only did the steel corrode to a greater extent than the iron, but the difference is so slight that for all practical purposes it can be said that the steel and iron of the experiments (ship-plates) were equally affected. They also confirm the theory that the combination of steel and iron, which is quite frequent in practice, is detrimental to the iron, but protects the steel which is the negative partner. They also throw light on previous observations, and lead to the conclusion that good homogeneous iron and steel are about equally corrodible."

Mr. J. P. Snow, Chief Engineer of the Boston and Maine Railroad, has called attention to a very significant case of corrosion in connection with the destruction of some railroad signal bridges erected in 1894, and removed and scrapped in 1902. These structures were built at the time that steel was fast displacing puddled iron as bridge material. The result was that the bridges were built from stock material which was partly steel and partly wrought iron. The particular point of interest in this case lies in the fact that while some of the members of the bridge structures rusted to the point of destruction in eight years, others were in practically as good condition as on the day they were erected. This is clearly shown in the illustration, page 8, which is from a photograph of these bridge members. The specimen shown in the middle has suffered only very slight superficial rusting, while those shown on either side have gone to the point of destruction. Tests carried on by Snow and examinations made by one of us appeared to indicate that the badly rusted parts were steel and the unrusted portion wrought iron. On first thought this observation would appear to indicate that wrought iron was far superior to steel as material for such structures. In the light of the electrolytic theory and of the other evidence that has been given, it appears highly probable that the steel in this case was electro-positive to the iron, which resulted in the protection of one metal at the expense of the other.¹ From this

¹It should be noted that the equilibrium which decides which metal will be positive to the other is a delicate one and is determined by a number of factors, which may or may not be known.

point of view the steel is no more to be condemned for having failed than the iron for having been the destructive agent. With the results of recent investigations to guide them, it is not probable that engineers will permit the assembling of different types of metal in one and the same structure, without first considering the probable effect on its life.

Effect on Corrosion of Other Constituents in Steel. — We have now to consider the influence on corrosion of the other usual impurities found in steel, such as manganese, phosphorus, sulphur, and silicon. From the standpoint of the electrolytic theory there are several reasons why the presence of manganese in steel should invite corrosion. Manganese decreases the electrical conductivity of iron, and as the percentage of manganese, starting from zero, rises, the electrical resistance increases up to a certain specific maximum. It will be seen that if the presence of manganese in iron raises the electrical resistance, any variation in the distribution of the manganese means that there will not be a constant electrical conductivity throughout its mass, or on any given surface. There is abundant evidence to show that manganese associates itself to a considerable extent with sulphur when both these impurities are present in steel.¹ That manganese sulphide shows a difference of electrical potential against iron is also well known. These theoretical reasons which indicate that manganese should stimulate the corrosion of steel, provided it is not perfectly homogeneously distributed in the iron, appear to be justified by a number of reliable observers among whom may be mentioned Dudley,² Drown,³ Abel,⁴ and Reynolds.⁵ Huntley⁶ deals with the corrosion of boiler steel, and gives details of a case of pitting in a boiler. Each pit was found to be the center of a blister, and the blister contained a slightly acid solution of ferrous sulphate, while the boiler water was alkaline with caustic soda. The solid matter in the envelope of the blister, which consisted of a mixture of iron oxides, acted as a semi-permeable membrane, keeping apart the ferrous sulphate within and the caustic soda outside the blister. The theory advanced is that the particles of manganese sulphide, segregated

¹ Fay and Howard, Trans. Am. Soc. Testing Mat., 1908, 8, 74.

² Trans. Am. Inst. Mining Eng'rs, 1905. Disc. Roe's paper.

³ *Ibid.*

⁴ Proc. Inst. C. E., 1881.

⁵ *Ibid.*

⁶ Jour. Soc. Chem. Ind., 28, pp. 339-340.

in the steel, were oxidized by the oxygen dissolved in the boiler water to sulphuric acid and an oxide of manganese, the acid then acting locally on the surface of the boiler plate in the vicinity of the particles of manganese sulphide. The pitting of the boiler plate was prevented by adding sodium arsenite to the boiler water, the reagent taking up the dissolved oxygen.

It should be noted that the above discussion refers to manganese when it occurs as an impurity in steel in amounts not exceeding about 1 per cent. Very high manganese steels are said to be unusually resistant to corrosion. It must be remembered, however, that in the latter case we are not dealing with steel at all, but with one or more special alloys in which stable eutectics are probably formed. These special manganese alloys would then fall in line with many others which are very well known to be highly resistant to corrosion. Among these resistant alloy steels that have been noted we may mention nickel,¹ chromium, vanadium, tungsten, and silicon. More systematic investigation of this subject is needed.

Phosphorus has been claimed to render iron more resistant to corrosion, but actual information in the literature of the subject is too meager to found an opinion on. Sang² says: "Phosphorus and silicon both appear to retard corrosion, and this effect may, as in the case of carbon, have some connection with their hardening qualities, or cold-shortening power. If, however, they are present in patches, like the oft-occurring phosphide eutectics, the softer parts, through contact action with the parts rich in phosphorus and silicon, will be destroyed all the more rapidly. Some authors have claimed that these two elements increase corrosion, but there is no evidence to support the contention apart from the case of uneven distribution which will make any of the impurities rust promoters to a greater or lesser extent. The fact that common iron does not rust as rapidly as the better grades has been attributed by some to the greater percentage of phosphorus in the former."

Sulphur is usually present in steels in very small quantities, and probably affects the rate of corrosion mainly by increasing segregation, as in the case of manganese sulphide already cited.

Silicon in small quantities like manganese may increase

¹ Unger, Proc. Eng. Soc. of West. Pa., 24, 10, 549.

² *Ibid.*, page 259.

the tendency to corrosion. In larger quantities from 10 to 20 per cent., the solubility in acids as well as the tendency to rust is checked. Jouve¹ has called attention to the fact that iron containing 20 per cent. of silicon is not attacked by acids, and therefore such material theoretically should not be subject to rust. One of the authors has confirmed this deduction by experiment, and found that iron containing more than 10 per cent. of silicon is almost incorrodible. Unfortunately, such a metal is not easily workable and has peculiar properties. Since silicon is much like carbon, chemically speaking, it would seem as if it might be worked into the surface of steel by modifications of some of the processes used for case-hardening with carbon.

Various Factors which Modify Effect of Impurities. — It will be readily understood that even if there were much more data available than we have it would be quite impossible to accurately state the influence that any given impurity will have upon the corrosiveness of iron. Not only will much depend upon the quantity, distribution, and condition of the impurity, but the balanced effect produced by other impurities is an ever present factor in a heterogeneous equilibrium. The discussion and citations given in preceding paragraphs have been included only inasmuch as they have a bearing on the electrolytic theory of corrosion. But even as the interior structure of a metal influences its tendency to corrode, its use in connection with other types of metal in construction work becomes a matter of even greater importance. This has been pointed out in regard to iron of varying carbon contents.

Problem of Combining Structural Metals of Different Chemical Constitution. — If two metallic elements are joined in a structure the more electro-positive one will be corroded rapidly, while the more electro-negative will be protected. It therefore follows that even if a complete knowledge of the chemical constitution and interior structure of a metal was in our hands, unexpected results might still be met with under service conditions. A case in point is shown by the work of Preuss.²

In order to study the influence of electrolysis, a number of nickel steel rivets and iron rivets were driven through several plates of mild steel, and immersed for two months in a brine

¹ Engineer, 1908, 106, 397.

² Iron and Steel Inst., Carnegie Scholarship Memoirs, I, 1909, p. 81.

corresponding to sea-water. The loss in weight sustained by the nickel steel rivets, as compared with the loss sustained by the rivets of iron, was in the proportion of 11 to 6. As the nickel steel was essentially more uncorrodible than the iron, we see in this a reversal of resistibility which only a complete understanding of the principles of electrolysis can explain. Sang cites the work of Mallet which is interesting in this connection.¹

"The effects of electrolytic action are clearly demonstrated by the results secured by Mallet in a series of experiments which he undertook in order to ascertain the 'amount of corrosion in equal times in clear sea-water of a unit surface of wrought-iron plate, exposed in electro-chemical contact with an equal surface of the following metals electro-negative to it, as compared with the corrosion of the same surface of the same iron exposed *alone* for the same length of time;'

	Relative Corrosion
Iron plate alone.....	8.63 per cent.
In contact with: Brass ($\text{Cu}_2 + \text{Zn}$) ...	29.64 " "
Copper.....	42.79 " "
Lead.....	47.90 " "
Gun-metal (Bronze).	56.39 " "
Tin.....	74.71 " "

"In connection with the above table, the valuable fact is mentioned that the brass alloys of composition, $\text{Cu}_8 + \text{Zn}_{17}$ to $\text{Cu}_8 + \text{Zn}_{18}$, are without galvanic action on iron in sea-water. This explains the incorrodibility of the alloy of iron, copper, zinc (and sometimes tin), which is known as Delta metal, and which, tested in conjunction with wrought iron and steel, showed remarkable resistance under test, as follows:

	Wrought Iron	Steel	Delta Metal
Loss.....	45.9	45.45	1.2 per cent.

"The first copper-zinc alloy for the special purpose of resisting the action of sea-water was patented in 1832 by Muntz. Muntz metal is used for bolts, valves, etc., and for sheathing ships; its composition is 2 parts zinc to 3 parts copper. Tobin bronze is similar to Delta metal, but contains tin and lead."

Walker has used the ferroxyl test to give some very pretty illustrations of the protection of the electro-negative element

¹ Proc. Eng. Soc. West. Pa., XXIV, 10, p. 521.

in an electrolytic couple. This is shown in Fig 21, where iron is suffering from stimulated corrosion owing to its being in connection with the more electro-negative metal platinum, while in Fig. 22, the reverse action is taking place, the iron being protected by contact with the more electro-positive metal zinc. In Fig. 23 the accelerating effect of the electro-negative mill-scale or magnetic oxide is shown.

Conclusions Based on Measurements of Potential Differences.—In view of the fact that differences of potential are known to exist not only between metals of different types, but also on the surface of more or less homogeneous pieces of iron, it is natural that a number of experimenters should have attempted to measure them. Unfortunately, these attempts have led to results of little or no value. As a matter of fact the equilibrium is so delicate that the slightest disturbance has an influence on the electric potential, which is always subject to change owing to more or less obscure causes over which little or no control can be exercised.¹ Some experimenters have made elaborate series of potential measurements which have led them to conclusions, without apparently understanding that the measurements were in reality nothing but haphazard results, which should not be interpreted as leading to definite conclusions. In many cases such results have been largely effected by the potentials of the contact points between the metals under examination and the take-off wires of the measuring instruments. Walker's² ingenious method of adapting the potentiometer to the measurements of potential differences on the surface of iron was published some years ago, but this authority has since concluded that even these carefully made measurements cannot be used either to support or refute the electrolytic theory of corrosion. In the hands of nearly all investigators the efforts to establish definite polarity between samples of steel of different chemical analysis have led to confusing and unintelligible results. In one investigation which came under the notice of one of the authors, the effort was being made to measure the difference of potential

¹ Compare: Punga, *Mitteilungen aus dem Material Prüfungsamt zu Gros-Lichterfelde West*, 1908; See also Prens, *Iron and Steel Inst.*, Carnegie Memoirs 1909, I, 82.

² Walker, Cedarholm and Bent. *Jour. Am. Chem. Soc.*, XXIX, 9, 1263 (1907).

between two steel wires. One wire contained .50 carbon and .81 manganese, the other .50 carbon and .40 manganese. These were cleaned and polished and after being connected with an astatic galvanometer were plunged part way into a very dilute acid electrolyte. The galvanometer needle deflected 15° to the right, indicating that the low manganese was electro-positive to the high manganese wire. In another test of the same samples, made after the wires had slightly corroded, the needle deflected 60° to the left, indicating that now the low manganese was strongly electro-negative to the higher manganese wire. In experiments made by one of the authors in which steel electrodes have been connected with a battery current of very low e.m.f. and amperage and plunged into ferroxyl indicator, blue spots have been seen to form underneath the pink envelope on the negative electrode. Such an appearance serves as an ocular demonstration of the delicacy of the equilibrium since it is thus shown that a negative member in an electrolytic couple can develop a superimposed polarity of its own. The same effect can be seen by close inspection of Fig. 11, page 53, although in this case the pink zones are not being controlled or demarked by an external current. In calling attention to these anomalous effects, the authors merely wish to suggest that the results obtained from delicate measurements of polarity should be used with caution in drawing conclusions.

Effect of Heat Treatment, Tempering, Stresses, Strains, etc. — The effect of heat treatment probably has as much to do with the resistance tendency to corrosion as any other factor to the problem. Under the special caption of heat treatment we may include all effects produced by rolling, whether hot or cold, as well as surface stresses and strains. This subject has been investigated by a number of authorities. Andrews¹ has published a paper on tests of steel under tensile, torsional, and flexional strains, and found that the unstrained parts were electro-positive to strained parts. Hambuechen,² following more or less closely the method of Andrews, arrived at a diametrically opposite result, and concluded that the strained metal was electro-positive, and hence would corrode more rapidly. Both of these investigations were unsatisfactory, and have been criticized by Walker and

¹ Proc. Inst. C. E. (1894), 353.

² Bull. Univ. Wisconsin, Engineering Series 8 (1900).

Dill.¹ Richards and Behr² included some interesting experiments upon the effect of strain upon the potential of iron. No definite conclusion was reached, but it was clearly indicated that if potential differences exist, the equilibrium that governs them is an extremely delicate one. Walker and Dill³ were led to believe that although the potential differences were small, the strained metal had a slightly less tendency to corrode than the same metal unstrained. Burgess⁴ has concluded that test pieces that have been deformed by straining beyond the elastic limit show a measurable difference of potential. That the potential equilibrium is a delicate one is again indicated by the fact that Burgess's strained parts corroded faster than the unstrained. This observation is confirmed by a great number of ferroxyl tests in which the deformed or strained portion of a specimen is usually electro-positive and shows up in blue. It is for this reason that the heads and points of wire nails are usually electro-positive to the middle portion in ferroxyl tests. This is not invariably the case, however, as may be seen in Fig. 10. The exception to the general rule only serves to show that strains set up in the cold-drawing of the wire from which the nails are fabricated has reversed the polarity.

It appears to the authors that these apparently contradictory results arrived at by different experimenters may be best explained by the extreme delicacy of the equilibrium which governs the polarity. That iron has a definite solution pressure has already been shown. If for any reason, however obscure, the solution tension is to any extent greater at one point on a given surface than at another, that point will be to some extent electro-positive to the other. Whether these points retain the polarity or whether it is actually reversed depends upon the nature of the given case, in which determinative causes may be at work which it is impossible to predicate.

Sang⁵ makes the following observations in reference to this subject: "Some years ago Witkowski⁶ found that in a strained

¹ Proc. Am. Soc. Testing Materials, VII, 230.

² Publications Carnegie Institution, Washington (1906).

³ *Loc. cit.*, p. 237.

⁴ Trans. Am. Elec. Chem. Soc., 1908.

⁵ Proc. Eng. Soc. West. Pa., XXIV, 10, p. 513.

⁶ Trans. Roy. Soc. Edin., vol. XXX (1881), p. 413.

metal there is an increase of electrical resistance in the direction of the strain. All these observations go to prove the claim that mechanical treatment, by setting up uneven strains in different parts of finished pieces, will create variations of potential which will promote rusting. Whatever the composition of the different inner parts of the metal may be, and apart from any action which may be due to difference of composition, if there is a difference of molecular aggregation, it will promote the rusting of one or other of those parts. Action, power, everything knowable, depends on difference of potential, and any chemical or physical difference between two portions of matter in contact must give rise to a difference of potential and a flow of electricity.

"If straining a metal below its elastic limit by exteriorly applied mechanical means will make it electro-negative to the same metal unstrained, the strains set up by chilling or hardening should have a like effect; the metal should resist corrosion to a greater extent and promote the corrosion of more positive metals in contact with it. This is found to be the case. Eighty years ago Daniel observed that a certain steel was dissolved by hydrochloric acid five times as rapidly when unhardened as when hardened; this is an indication of what we may expect with the agents of corrosion. What becomes of the energy of a coiled watch spring when it is dissolved in acid? This is supposed to be one of the many unsolved mysteries of science. The energy of the coiled watch spring is indicated by a slight shift of its potential towards the negative end of the electro-chemical scale, resulting in an increase of e.m.f.; when the spring is put in acid, the energy is expended in retarding the action of the acid, and is equivalent to a drop of temperature which would restrain chemical action. The energy of the spring, as increased e.m.f., counteracts the energy of the acid, is expended and disappears as work of a negative character."

Relative Stability and Solubility of Strained and Annealed Metals. — A most interesting paper by Heyn and Bauer¹ on the influence of heat treatment on the solubility of steel in sulphuric acid throws much light on the effect of such treatment on the resistance character and stability of steels. This paper should be carefully studied by all who are interested in the manufacture of rust-resistant steel, for it very clearly shows the relative sta-

¹ Jour. Iron and Steel Inst., 1, May, 1909.

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bility of strained and annealed metals. In view of the importance of this work and its direct bearing on the subject under discussion, the following citations from these authors are worthy of record.

"In the experiments a tool steel with the following composition was first used:

	Per cent
Carbon	0.95
Silicon	0.35
Manganese	0.17
Phosphorus	0.012
Sulphur	0.024

It was in the form of a square forged bar of a cross-section 25×25 millimeters. From this bar sections of a thickness of 6 millimeters were cut and subjected to the following treatment:

- (a) Heated to 900°C. , and quenched in water at 14° to 18°C. , untreated
- (b) " " " " " reheated at 100°C.
- (c) " " " " " at 200°C.
- (d) " " " " " at 275° to 305°C.
- (e) " " " " " at 405° to 415°C.
- (f) " " " " " at 500°C.
- (g) " " " " " at 600° to 640°C.
- (h) In the original forged state.
- (i) Heated to 900°C. and allowed to cool slowly.

"The high quenching temperature of 900°C. was chosen for the reason that with a small test-piece pure martensite is obtained by quenching in cold water and observing the necessary precautions. At lower temperatures those constituents indicating the transition to troostite occur in addition to martensite, and mark the observation. After the treatment as described above, the sections of an area of 25×25 millimeters were polished and immersed with the polished surface uppermost in 1 per cent. sulphuric acid. The weight before immersion, and the loss in weight at the end of twenty-four, forty-eight, and seventy-two hours respectively, were determined. In Fig. 24 the tempering temperatures are taken as abscissæ and the respective losses in weight as ordinates.¹ The letters attached to the ordinates refer to the kind of treatment given in the foregoing table. For the sake

¹ For more detailed information see E. Heyn and O. Bauer, "On the Structure of Quenched and Tempered Tool-steel," etc. (Communications of Royal Inst. for Testing Materials at Gross-Lichterfelde, 1906, p. 29.)

of clearness the separate values are omitted, and only the average values of several experiments are given.

"The shape of the curve in Fig. 24 reveals some startling features. According to the opinions hitherto prevailing, and still held by some, the transition of the martensite of hardened steel into the pearlite of annealed steel is continuous throughout the intermediate states of tempering. This would lead one to sup-

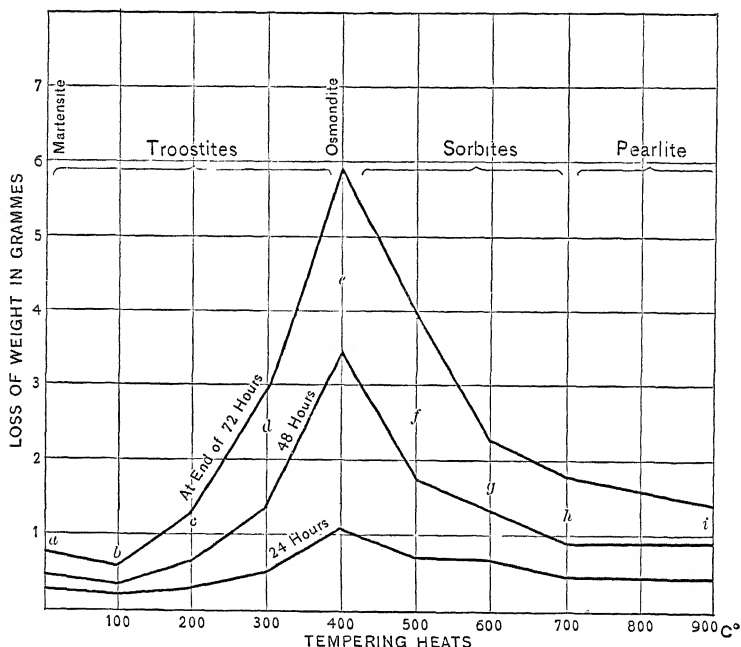


FIG. 24.- Tool steel in various states of heat-treatment. Solubility in one per cent. sulphuric acid. (Heyn and Bauer.)

pose that the curve of solubility in dilute sulphuric acid, instead of showing any sharply defined peaks, would form a line indicating the gradual transition from the solubility of martensite to that of pearlite. The curve, however, runs up to a sharply defined maximum at a temperature of 400° C. The simplest and most obvious explanation of this phenomenon is as follows: The transition of the martensite from the unstable phase below 700° C. into the stable phase of pearlite, due to tempering, does not proceed directly, but indirectly through an intermediate

metastable form, to which the name osmondite has been given by the authors in honor of the celebrated investigator Osmond. Osmondite is the most soluble of all the forms intermediate between martensite and pearlite. As the tempering temperature gradually increases, the martensite first gradually changes into osmondite, until at 400° C. the whole mass consists of this alone. In order to prevent confusion in nomenclature, the term troostite has been hitherto retained by the authors for the designation of the intermediate states between martensite and osmondite, and for the stages intermediate between osmondite and pearlite they have continued to use the term sorbite. If the tempering temperature is raised above 400° C. there again occurs a gradual transition from the readily soluble osmondite to the less easily soluble pearlite. Such transitions from a preliminary condition to a stable final condition, through one or more less stable intermediate conditions, are of not infrequent occurrence in physical and chemical processes. As an instance may be mentioned the combustion of hydrogen, which, according to Nernst,¹ is not burnt direct to water, but proceeds indirectly through the medium of the less stable peroxide.

"Another remarkable point in Fig. 24 is the lowest value for the solubility at a tempering temperature of 100° C., which differs little from that of untempered steel. The variation lies, however, within the margin of error for the process, so that whether still another metastable intermediate form occurs is not yet proved."

Similar work carried out on a sample of pure mild steel is recorded by Heyn and Bauer as follows:

"The Influence of Quenching and Reheating Soft Mild Steel upon its Solubility."

"For the experiments a very low carbon mild steel was used, of the following composition:

	Per Cent.
Carbon	0.07
Silicon	0.06
Manganese	0.10
Phosphorus	0.01
Sulphur	0.019
Copper	0.015

The material was in the form of a rolled square bar 25 × 25 milli-

¹ Zeitschrift für Elektrochemie, 1905, Vol. II, p. 713.

meters in cross-section. From this bar were cut transverse sections $23 \times 23 \times 6$ millimeters, which were polished bright on an emery wheel. Near one corner a hole was bored, by which the small plates were suspended on glass hooks in the dilute sulphuric acid.

"The test-pieces were quenched from a temperature of 1000° to 1030° C., since mild low carbon steel first becomes homogeneous

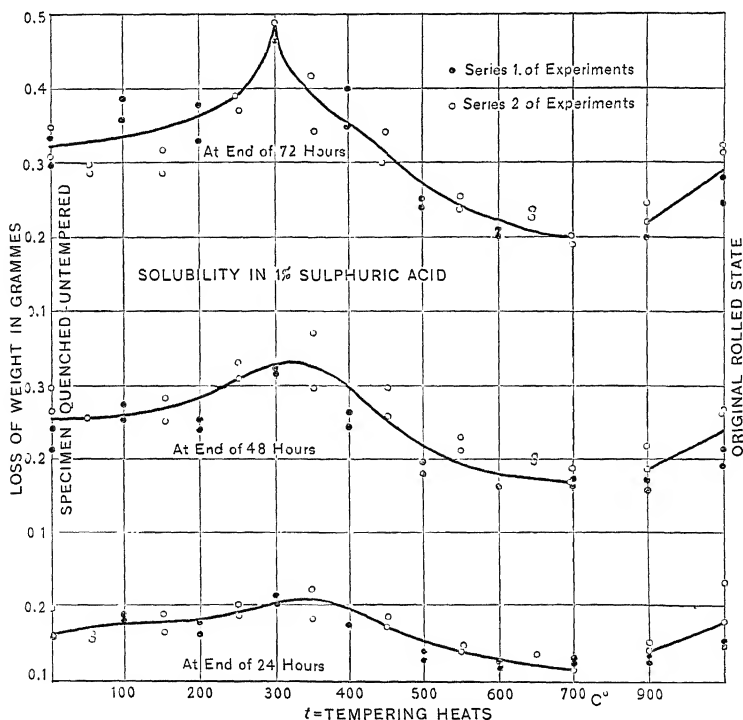


FIG. 25. — Mild steel, carbon .07 per cent., quenched at 1000° degrees to 1030° degrees centigrade in water at 18° degrees centigrade; tempered for two hours at (t) degrees centigrade. (Heyn and Bauer.)

from 900° upwards. The duration of reheating was two hours, and it was effected at the temperatures t given in Fig. 25. As a rule, at the end of the two hours the specimens at t° were quenched in water for the purpose of suddenly interrupting the tempering effect. Only the specimens reheated at 700° were first cooled slowly to 690° , that is, below the critical temperature 700° , and

then quenched, otherwise a new quenching effect would have been added. The samples reheated at 900° were cooled quite slowly to the temperature of the room.

"The loss in weight in 1 per cent. sulphuric acid was determined in two series of experiments (I and II), which were carried out independently of one another. The Roman numerals against the numbers of the test-pieces in the table indicate to which series the particular experiment belongs.

"The test-pieces were suspended by means of glass hooks on glass rods, the hooks being passed through the holes. They were entirely immersed in the acid without being in contact with each other. The quantity of attacking liquid was 2500 cubic centimeters for every ten to eleven test-pieces. The following are the numbers of the test-pieces which were placed together in the respective vessels:

SERIES I. — TEST-PIECES

Vessel A.....Nos. 1, 3, 5, 7, 9, 11, 13, 15, 17, 52

Vessel B.....Nos. 2, 4, 6, 8, 10, 12, 13, 16, 18, 53

SERIES II. — TEST-PIECES

Vessel A.....Nos. 19, 22, 27, 30, 38, 41, 44, 54, 57, 60, 62

Vessel B.....Nos. 20, 23, 28, 34, 35, 39, 42, 50, 55, 58, 63

The two series of experiments I and II were undertaken at different times. In each series the test-pieces in both vessels A and B were exposed to the action of the acid at the same time and in the same room. The results of the two series are, however, not immediately comparable, because the temperatures were not observed; nevertheless they have been amalgamated for the sake of clearness in Fig. 25. The losses in weight, in grams, at the end of twenty-four, forty-eight, and seventy-two hours' immersion in the acid, have been entered in the diagram. In the curve the points relating to Series I are marked thus, ●, and those relating to Series II, thus ○. The tempering heats are taken as abscissæ, and the losses in weight as ordinates.

"A maximum degree of solubility is plainly noticeable between the reheating temperatures 300° and 400° , which again correspond to osmondite. Thus this intermediate constituent, even with so low a carbon content as 0.07 per cent., still shows its special characteristic of greatest susceptibility to attack by the acid. "On comparing Fig. 25 with Fig. 24, it will be observed

that in the case of the hard steel the solubility of the test-piece, with a degree of temper = 0 (martensite), is lower than that of the slowly cooled steel with degree of temper = 1 (pearlite). With the mild steel, on the other hand, the solubility of the untempered test-piece is greater than that of the fully annealed one. This is no matter for surprise, since it is not possible with mild low carbon steel, however suddenly quite small samples may be quenched, to obtain martensite—that is, the degree of temper = 0."

Influence of Wire-drawing and Subsequent Annealing.—The work of Heyn and Bauer on the influence of wire-drawing and subsequent annealing is particularly suggestive. For the details of this work the original should be referred to. Some of the conclusions reached are as follows:

"1. By cold-drawing the wire, the solubility of the mild steel is increased. It rises rapidly until the ratio of elongation $N = 4$ is reached, but drawing beyond that point produces comparatively little further increase of the solubility.

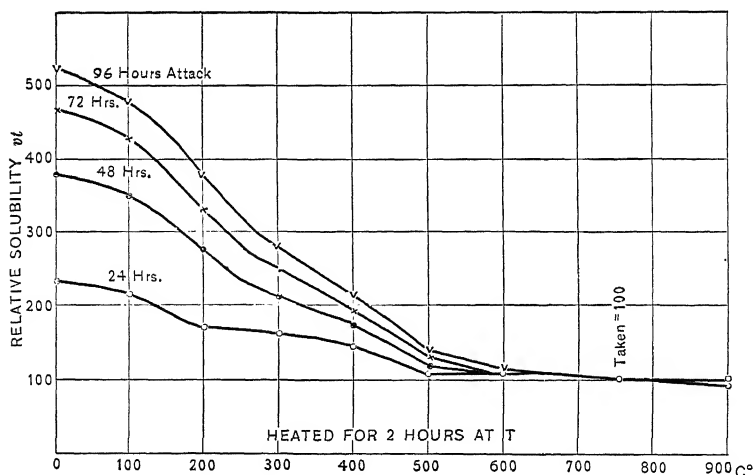


FIG. 26. — Influence of heating on the solubility of cold-drawn, hard wire. (Heyn and Bauer.)

"2. In the case of the harder wire, the curves of relative solubility for the different periods of attack lie nearer to each other than those of the softer wire, as may be seen from a comparison of Figs. 26 and 27. This means that the relative

loss of weight of the softer material is less during the first period of attack than that of the harder material, but that as the period of attack is prolonged, the loss of weight increases more rapidly in the softer than in the harder steel wire.

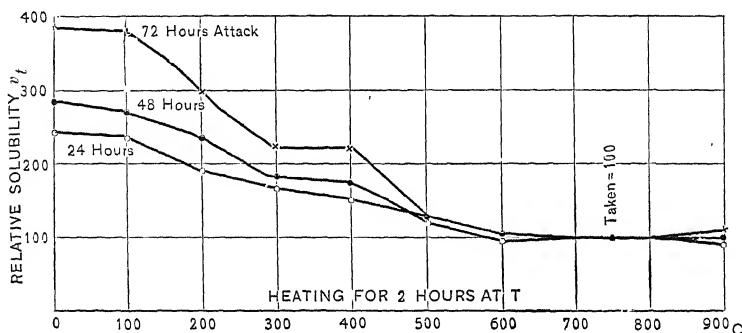


FIG. 27. — Influence of heating on the solubility of cold-drawn, soft wire. (Heyn and Bauer.)

"3. After annealing the wires drawn from the same mild steel material, the degree of solubility is immediately no longer affected by the cold-drawing of the wire, however far this may have been carried. Wire-drawing, therefore, produces no change in the material which cannot be removed by annealing.

"4. The heating of the cold-drawn wire involves a decrease in the degree of solubility (Figs. 26 and 27). The decrease in solubility is plainly noticeable even after heating to 100°."

Cold-working Increases Solubility of Mild Steel. — The solubility of mild steel is shown to be increased by cold-working, irrespective of whether the cold-working has been effected by stretching or compression. Part of this effect is shown in Fig. 28. The investigators considered the solubility of iron from the electrochemical point of view, and are led to assume that iron exists in some allotropic form induced by cold-drawing. They say:

"It has to be further investigated whether iron, with reference to the increase of its solubility by cold-working, occupies an exceptional position with respect to all other metals, or whether there are other metals which behave in the same manner. If the former is the case, then the increase in solubility of cold-worked iron can only be attributed to the presence of a more readily soluble allotropic form of the iron, which is produced by cold-working.

"Since the degree of cold-working does not require to be the same in all parts of the cold-drawn wire, one might then expect to find at different parts of it different quantities of the more soluble modification of the iron. This would explain why the surface of the drawn wire, on being subjected to the solubility test, becomes roughened, while the same wire after annealing preserves its smooth surface under the acid attack. The difference in the solubility might be accentuated if the galvanic effect differed of the parts subjected to varying degrees of cold-working. Investigations upon the electric potentials of cold-drawn and annealed wire in

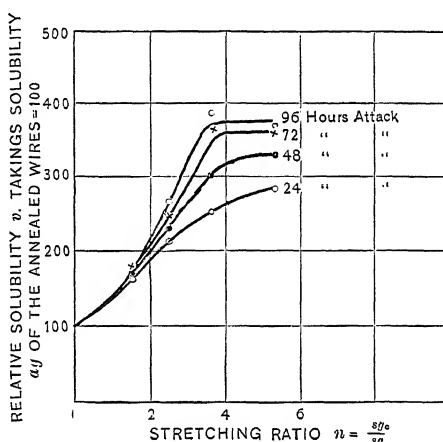


FIG 28. — Influence of cold-drawing on the solubility of mild steel wire. (Heyn and Bauer.)

contact with acid and solutions containing Fe ions were not undertaken by the authors. On the other hand, the differences of potential in distilled water were measured, and were found to be considerable, as appears from Fig. 29.

It cannot, however, be concluded from these figures that the potentials peculiar to the cold-drawn and annealed wire necessarily differ from each other, since what is measured in water is not the actual potential of the iron, but the potential of an oxygen electrode formed on the iron, which certainly does differ considerably as between cold-drawn wire and annealed wire. The oxygen electrode formed on the cold-drawn wire appears more electro-positive than that on the annealed wire, which

indicates that during the experiments the drawn wire consumed more oxygen, that is, it rusted sooner than the annealed wire.¹

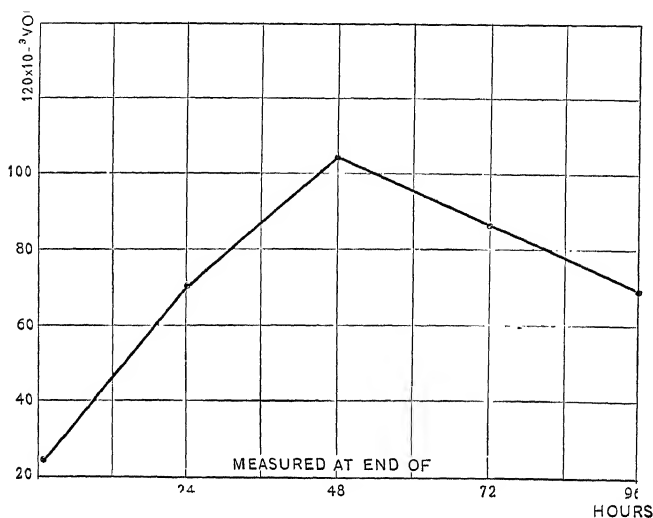


FIG. 29. — Electric potential drop between a cold-drawn hard wire and the same wire after annealing. Measured in distilled waters at 17 to 18 degrees C. The cold-drawn wire is poorer in quality than the annealed. (Heyn and Bauer.)

“Pairs of wires were prepared as follows: A piece of wire 100 millimeters long in the original cold-drawn state marked *u* was

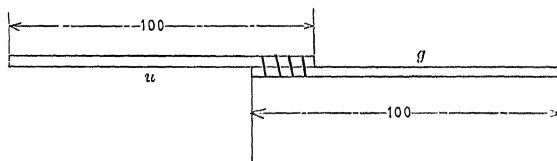


FIG. 30. — Pairs of wires connected together for rusting test. (Heyn and Bauer.)

attached as shown in Fig. 30, by means of platinum wire to another piece of wire marked *g*, annealed for half an hour at 900° C.

¹ E. Heyn and O. Bauer. “Über den Angriff des Eisens, etc.” “Mitteilungen aus dem Königlichen Materialprüfungsamtes.” Gross-Lichterfelde, Nos. 1 and 2, 1908.

These pairs were supported at their free ends on glass rods, and completely immersed in distilled water of about the warmth of the room. At the end of twenty-two and forty-nine days the losses in weight of the single wires due to rusting were ascertained, and in all cases it was found that the cold-drawn annealed wire was more strongly attacked than the annealed wire, the proportion being from 103:100 to 108:100. Whether this proportion remains unaltered or is reversed under a long exposure is not yet determined, but such a possibility is by no means precluded.

"100-millimeter lengths of the same kind of steel wires were then attached together in pairs in the same manner in order to see whether the attack on iron by dilute sulphuric acid (1 per cent.) was affected when cold-drawn and annealed wires were in metallic contact with each other. It appears that the strength of the sulphuric acid attack on the cold-drawn wire is increased by 1.19 to 3.3 times. Therefore if the degree of cold-working differs in different places in the same wire, the wire will be attacked unevenly, owing to the contact of the unequally worked parts, and moreover the attack on the most heavily worked will proceed quickest. This is the explanation of the furrows and roughnesses on the surface of the drawn wires after an acid attack, and the smooth nature of the surfaces of the wire annealed before attack.

"On the basis of the foregoing considerations on elastic and plastic change of form, the state of a cold-drawn wire might be compared with that of a structure produced in the following manner. Imagine a pressure cylinder filled with a thick fluid mass, for instance, pitch, and that mixed with this is a great number of small cylindrical helical springs. Pressure is then applied to the mixture, and it is forced out of the cylinder through a round hole. The pitch undergoes a purely plastic change of form, but the helical springs suffer an elastic change of form. As soon as the pressure from outside the mold ceases the springs have the tendency to return to their state of equilibrium, that is, to their unstrained state, but they are partly prevented by the mass of pitch surrounding them. Consequently they remain partially under stress, and the amount of this stress may vary in different parts of the mass. If one can imagine a similar condition with respect to cold-drawn wire, it is intelligible why the amount of the elastic stresses varies so greatly at different parts."

The Acid Test as a Measure of Corrosion Resistance. — This interesting discussion opens up the important question of the use of an acid test as a measure of corrosion resistance. This test has been much used by some manufacturers who believe it to be reliable as an accelerated method for measuring the stability and hence the corrosion resistance of their products. The applicability of the acid test is absolutely denied by some authorities,¹ and is treated with caution by others.² Committee U of the American Society for Testing Materials has reported that the acid test should not be used to decide the relative resistance to corrosion of different types of iron and steel, but since it seemed necessary that investigators should use the test in the same way, the following tentative suggestions for carrying it out were made:

Samples to be tested are first stamped with suitable marks for identification, and are then accurately machined to a standard size, 2 inches in length, $\frac{1}{2}$ inch in width, and $\frac{1}{16}$ inch in thickness.

The samples should be cut longitudinally in the direction in which the metal was rolled. A hole $\frac{1}{8}$ inch in diameter is drilled in each sample about $\frac{1}{4}$ inch from one of the ends.

Samples are polished first with No. 00 emery paper, and finally with flour emery. The polishing should be done as much as possible, so that the polish marks run at right angles to the direction in which the metal was rolled. After polishing, the test pieces should not be handled with the fingers or allowed to come in contact with dirt or grease of any kind.

The test-pieces should then be weighed carefully to four decimal places on a chemical balance, and are then strung on a glass rod with a double reverse right-angle bend at each end, which will allow the pieces to be suspended in a relatively large beaker or other suitable dish, so that their upper edges will be submerged to $\frac{1}{4}$ inch below the surface of the liquid. The glass rod should be only slightly less than $\frac{1}{8}$ inch in diameter, and the distance between any two adjacent test-pieces when suspended in the acid should not be less than $\frac{1}{2}$ inch.

The acid should be exactly 20 per cent. H_2SO_4 (1.144 specific gravity at 15° C.).

The test-pieces are immersed in this acid for one hour, an approximately sustained temperature of 15° C. being maintained

¹ Saniter, Jour. Iron and Steel Inst., LXXIX (1909), p. 98.

² Speller, Proc. Eng. Soc. West. Pa., 24, 10, 541, Jan. 1909. Sang., Ibid.

by any suitable cooling device, such as a large outside container of cold water.

At the end of exactly one hour's immersion the test-pieces are quickly removed from the acid, well rinsed with running water, wiped as dry as possible and kept for one hour in a desiccator over sulphuric acid before weighing.

The results should be recorded as actual and not as percentage loss.

NOTE 1. — It has been shown that the corrosion of the sample is not directly proportional to the area exposed. Hence it is essential in making comparative tests that a standard size be adopted.

NOTE 2. — Should the samples for investigation be less than $\frac{1}{16}$ inch in thickness, the other dimensions should be adhered to as closely as possible.

NOTE 3. — The physical condition of the surface of the sample is found to materially affect the rapidity of its solution. It is therefore desirable to finish all samples in the same way.

NOTE 4. — The strength of sulphuric acid chosen is that concentration which contains approximately the maximum number of hydrogen ions, and which experiments have shown to be the most suitable.

NOTE 5. — It is necessary that the samples be suspended in a reasonably large body of acid in order that the ferrous sulphate formed by the reaction may sink to the bottom or be otherwise dissipated through the solution, so that the concentration of the acid in the immediate vicinity of the samples be not materially changed.

NOTE 6. — The greatest care should be taken to employ only chemically pure sulphuric acid. It has been shown that very minute traces of arsenic, for example, seriously retard the rapidity with which iron is dissolved.

The Relation between the Acid Test and Resistance to Corrosion. — The authors of this work are not willing to state that the stability of a steel as measured by an acid test bears no relation to its long-time resistance to corrosion. Nevertheless the test has not shown itself reliable when used to distinguish between the rust-resistant qualities of samples of different types of iron and steel. The authors are in complete agreement with the following opinion of Heyn and Bauer:¹

"It is quite apparent that the chemical composition of iron

¹ Jour. Iron and Steel Inst., 1, 1909, p. 185.

must considerably affect the solubility in dilute sulphuric acid, and that the influence of the composition may equal or exceed in magnitude the influence described in the previous sections. It must therefore again be specially emphasized that the comparative tests of which particulars have been given only apply as regards their results, subject to the elimination of the influence of the chemical composition as an unknown variable. The whole of the solubility tests lead to relative results only, and the absolute degree of solubility has no special value. Only the relative values of the solubilities of the same material in various states of treatment are to be regarded as useful in throwing light upon the present state of the metal. But it is unsafe to draw from the behavior of one metal conclusions as to the behavior of another, even though their chemical compositions may be very similar, since it is always possible that such substances as are not determined in the course of analysis exercise an effect upon the solubility."

To the above may be added the now well-known fact that very slight amounts of certain impurities in the acid used produce wide variations in the quantity of iron dissolved in unit time. Very small quantities of arsenic contained as an impurity in the acid will check the solubility of iron to an extraordinary degree,¹ and this is probably true of many other sometimes unknown and unsuspected impurities. This fact is readily accounted for by the electro-chemical theory of corrosion. As has been previously explained, corrosion is a surface action and solution in acid depends upon the rapid depolarization and disengagement of hydrogen from the surface. This depolarization is easily affected one way or the other by impurities in the metal, and also in the electrolyte which provides the attack. It is not to be expected that the rapid attack furnished by a dilute acid will be comparable to the slow rusting of iron under the conditions of service. In the former case depolarization and solution go on rapidly, whereas in the latter case the difference of potential between positive and negative points and nodes on the surface is stubbornly maintained for long periods of time. Unfortunately the same considerations must apply to all the acceleration tests that have been proposed and used by engineers and metallurgists, such as aerated brines and natural waters through which air and carbonic acid are bubbled.

¹ Burgess, *Electro-Chem. and Met. Ind.*, IV, 384.

Probably No Reliable Acceleration Test Possible. — Owing to the nature of corrosion it is probably true that no perfectly reliable acceleration test for corrosion resistance can be devised. Corrosion, in the natural process of rust formation, that is to say, in very slightly acid media, is a question of comparatively slow growth under special conditions, and any effort to hasten the action changes all the conditions of equilibrium, producing an entirely different order of phenomena.

Nevertheless, evidence has been brought out in the preceding paragraph to show that stresses and strains as the result of cold rolling or imperfect annealing of steel will affect not only the degree of solubility in acid, but also the tendency to maintain differences of surface potential affecting the rapidity of corrosion. In view of this it is probable that when its limitations are understood and its results properly interpreted, the acid test will be useful in the hands of competent investigators.

Efficient Annealing Essential to a Rust-Resistant Metal. — A careful reading of the preceding paragraphs should show that in order to produce the most rust-resistant steel, it is not sufficient to work towards purity of the metal and homogeneous structure, but also efficient annealing as the last stage in the preparation of the product is absolutely essential. Recent work would appear to show that the annealing temperature necessary to remove the stressed condition is not high, provided sufficient time is allowed for equilibrium to be reached.

Effect of the Rusting Medium, Electrolytes, Natural Waters, etc. — In regard to two points all investigators are agreed, and as these furnish some common ground it is interesting to record them. Iron cannot rust in air or oxygen unless water is present, and on the other hand it cannot rust in water unless oxygen is present. The products of the combustion of coal, consisting, as they do, largely of carbonic and sulphurous acids, aggravate the corrosion problem for railway engineers, and in the neighborhood of large cities. It follows from what has been written in the previous paragraphs that any acid in the atmosphere or the water by which iron is environed will increase corrosion. In very damp climates the conditions are aggravated, and on the Isthmus of Panama they are said to be particularly bad. Natural waters do not all behave in the same way, some making a much more rapid attack on iron and steel than others. Sea-water, as is well

known, stimulates corrosion, as do also all acid mine waters. These results are easily explained by the electrolytic theory of corrosion. Provided that the dissolved ions do not actually inhibit the action, all dissolved salts which increase the electrical conductivity of the medium result in stimulated galvanic action and supply hydrogen ions. In some cases, however, it has been noted that brackish waters from rivers in which sewage flows is less active in promoting the pitting of boiler tubes than much purer waters. This fact merely serves to emphasize the conclusion that the speed of the action is functioned by the electrolytic solution pressure of the iron, and that in some cases the effect of dissolved impurities may be inhibitive instead of stimulative.

Highly Alkaline Solutions Prohibit Corrosion. — Iron does not rust in alkaline solutions which contain an excess of hydroxyl ions, that is to say, if the alkalinity is high enough, but in dilute alkaline solutions rusting goes on in a dangerous fashion, the tendency to pit being accentuated. This action is incompatible with the theory that free acid is necessary to induce rusting, but is explained by the electro-chemical theory. Hydrogen and hydroxyl ions can exist in a solution at the same time to a considerable extent only when they are separated or held apart by potential differences, and therefore in the rusting of iron the concentration of hydroxyl ions, or, in other words, the alkalinity, must reach a certain value before rusting is entirely prohibited. This is because, owing to the very slight dissociation of water, an excess of hydroxyl ions would be incompatible with the presence of free hydrogen ions.¹

Natural Waters May Contain Inhibitive Impurities. — In addition to hydroxyl ions there are many other impurities that may exist in natural waters to inhibit corrosion. It has already been stated that iron cannot rust in water unless oxygen is present, for although the first cause of corrosion is due to the electrolytic exchange between iron and the hydrogen ions, the presence of oxygen is absolutely necessary for the action to proceed. Walker develops the point as follows:²

¹After this paragraph was written the authors' attention was called to the fact that iron has a considerable solution tension in strong boiling alkaline solutions, but in such a case the equilibrium is reversed and the metal acts the part of a negative radical in conjunction with oxygen. This point is at present being investigated. See also Zincite, Chem. Zeit., 12, 355.

²Trans. Am. Electro.-Chem. Soc., XIV, 175 (1908).

"Since oxygen is necessary to insure the continuous removal of the hydrogen film, it is obvious that if no oxygen be allowed to reach the iron through the water, no corrosion can take place. This fact teaches us much regarding the corrosion of boiler shells and tubes. Pitting may be entirely avoided if the air be removed from the free water before its introduction into the boiler. This may best be done by the employment of an open feed-water heater, or, what is better still, a feed-water heater connected to the dry vacuum pumps of the condenser. If such treatment is not possible, the air may be removed from the feed water by drawing the water through a closed box containing scrap iron; the oxygen in the water is used up in corroding the scrap iron instead of the boiler tubes. Or, the oxygen in the water may be absorbed by feeding into the boiler with the water a very small quantity of an alkaline solution of a tannin material. Such a solution of alkaline tannate will break up under the pressure and temperature of the boiler, with the formation of a pyrogallate of the alkali, and this rapidly absorbs the oxygen. Soda ash, or rather alkali, is of course useful, but not because of its effect upon the oxygen content, but because, as has already been explained, corrosion is inhibited by thus decreasing the hydrogen ion concentration of the water."

Dissolved Oxygen a Stimulator. — A theory must inevitably be judged according to whether or not it furnishes a satisfactory explanation of observed facts. A subject so complex as the corrosion of iron furnishes many examples of recorded facts that appear on first thought to completely contradict each other in the light of the electrolytic theory. Such discrepancies, however, usually find a rational and simple explanation. The particular point under discussion furnishes a good example of just such a case. On first thought it would be assumed that the purer the water and the lower the electrical conductivity, the less will be the tendency to rapid corrosion. If it were possible to deal only with absolutely pure waters, this conclusion would undoubtedly be justified. Natural waters are, however, only more or less pure, so that the conditions necessary for corrosion to take place are always present, as far as this factor alone is concerned. When we further consider, however, that dissolved oxygen is a necessary and important factor in the corrosion problem, we get new light on the subject. Every sanitary engineer knows that the measure

of dissolved oxygen is a strong indication of the purity of a water supply. In sewage-laden natural waters, dissolved oxygen does not exist to any great extent, as the oxygen is fixed in oxidizing the organic matter present. The fact that certain impure waters have been found to be excellent boiler waters, thus finds a simple explanation under the electrolytic theory. It would not, of course, be safe to conclude that contaminated waters are less corrosive than pure waters, for this is far from being the truth. If two forces are present at the same time, acting in opposite directions, and if these forces are unknown and variable, it is impossible to tell what the resultant will be except by experiment under all the possible conditions. In the case in point, the impurity of the water should tend to increase the electrolytic action, but the absence of dissolved oxygen counteracts this tendency.

Relative Corrosion in Fresh Water and in Sewage.—In connection with what has been said above, Howe and Lodge's¹ exposure tests on wrought and cast iron plates are most interesting. These tests were carried out for the purpose of studying the efficiency of various protective coatings, but incidentally they serve to show the relative amount of corrosion which took place in fresh water and sewage.

LOSS OF WEIGHT OF WROUGHT AND CAST IRON WITH DIFFERENT PROTECTIVE COATINGS AND UNDER DIFFERENT CONDITIONS, IN POUNDS PER SQUARE FOOT OF SURFACE PER ANNUM.

Wrought-Iron Sheets (No. 32 Gauge, Black.)

Protective Coatings	Exposed to the Weather Inland		Immersed in —		Average
	Canada	New York State	Fresh Water	Sewage	
Bower-Barffed0	gain, .000.3	.006.7	.003.6	.002.5
Tinned	gain, .002.0	.000.1	.019.4	.007.1	.006.2
Nickel-plated0	.000.5	.050.4	.003.1	.013.5
Galvanized	gain, .000.4		.045.9	.080.5	.042.0
Barffed001.0	.003.1	.083.9	.117.0	.051.2
Black, <i>i.e.</i> unprotected	.001.3	.022.6	.137.0	.169.0	.082.5
Copper-plated000.2	.005.0	.179.0	.182.0	.091.6
Average	.000.02	.005.1	.074.6	.080.3	.040

¹ Howe, Metallurgy of Steel, 2d Ed. I, 372.

CAST-IRON PLATES.

Protective Coatings	Exposed to the Weather Inland		Immersed in—		Average
	Canada	New York State	Fresh Water	Sewage	
Bower-Barffed	gain, .004.0	gain, .003.1	gain, .005.5	.001.4	gain, .002.8
“ “ & paraffined000.6	.001.9	.000.2	.008.4	.002.8
Galvanized0	.0	.049.1	.061.0	.027.5
Tinned	gain, .003.1	.065.5	.061.0		.041.1
Nickel-plated	gain, .003.4	.002.5	.131.7	.083.3	.053.5
Copper-plated	“ .004.0	.005.0	.150.8	.119.2	.067.8
Black, <i>i.e.</i> unprotected	“ .006.3	.012.0	.148.3	.272.4	.106.6
Average	gain, .002.9	.002.1	.007.2	.086.7	.041

A single sheet of No. 23-gaged refined wrought iron was cut into plates 6 in. by 12 in., and others 6 in. by 6 in. Of the 6 in. by 12 in. pieces some were exposed without treatment of any kind, the scale left on; others were tinned; still others were galvanized by the Rhode Island Tool Company. Of the 6 in. by 6 in. plates some were Bower-Barffed by the Yale and Towne Company, others were Barffed by the Pratt and Cady Company, still others were nickel-plated and copper-plated, in each case after pickling. The cast-iron pieces were skin-bearing plates, 4 in. by 3.5 in. by 0.187 in., presented by Professor George W. Maynard. These were subsequently given the coatings indicated, their original skin being retained in all cases.

One set of the pieces thus prepared was exposed on the roof of a dwelling house in the Eastern Townships of the Province of Quebec, Canada, by Mr. E. C. Hale, of Sherbrook, Canada; a second was similarly exposed in a village in Rensselaer County, New York State; a third was immersed in the Chestnut Hill (Boston) Reservoir, by Mr. Desmond FitzGerald, of Boston; a fourth was immersed in the Boston main sewer, near the pumping station, by Mr. H. H. Carter, of Boston.

In each of the conditions of exposure the wrought-iron pieces were in one open wooden crate, the cast-iron ones in a second, the corners of the pieces (and in the case of the 6 in. by 12 in. wrought-iron pieces a small space in the middle of the long sides) alone being in contact with the crate; and care was taken that the specimens should not touch each other or any other metallic

substance. Though exposed nearly a year, including autumn, winter, and spring, at the end of the experiments the gummed labels still adhered to twelve out of the twenty-six specimens exposed in Canada and in New York.

The cast iron lost about as much as the wrought iron; the loss was about the same in fresh water and in sewage. Comparing the different conditions of exposure, immersion, of course, greatly accelerated rusting. Thus, in ten out of the fourteen sets of cases the pieces immersed in fresh water lost at least twenty times as much as those exposed to the weather in New York. The loss in sewage is slightly greater than in fresh water on the unprotected specimens, but in seven out of the fourteen cases the loss in fresh water equals or exceeds that in sewage, a result that was found difficult to explain before the electrolytic theory of corrosion was developed.

Non-Corrosion of Deeply Immersed or Buried Iron. — If it be admitted as a fact that both hydrogen ions and free oxygen are necessary to promote the corrosion of iron under the electrolytic theory, many curious instances which have been recorded of resistance to corrosion of iron which has been deeply immersed in water or buried deep in the earth are explained. If the zone of dissolved and active oxygen has been passed the zone of corrosion has likewise been passed, and the problem resolves itself into one of determining the limits of penetration of active oxygen. These conclusions should be considered in all cases where, as on the Isthmus of Panama, deep piling in engineering construction is contemplated.

Wemlinger¹ has collected some interesting data on this subject which we include here. "It has been stated that steel sheet-piling has often been used as a part of permanent structures, and the question naturally arises: What is the life of the steel sheet-piling embedded in the ground? In order to be able to fully answer this question, it is necessary to consider the various conditions that affect the durability of iron or steel in this case, such as the nature of the soil and the composition of the metal itself."

"In the first place, it must be remembered that iron or steel will not corrode in air unless moisture is present, nor will it corrode in water unless air is present.² Deep down in the ground the

¹ Engineering-Contracting, XXXI, 20, 407.

² Compare Cushman, Corrosion of Iron, Bull. 30, Office Public Roads, U. S. Dept. Agr.

amount of air dissolved in the water is almost nil, and it is only near the surface that the ground-water contains free air and carbonic dioxide carried down from the upper layers.

“There is every logical reason to believe that steel embedded in the ground or left in contact with standing water will be preserved indefinitely. However, it is appreciated that, no matter how much such evidence may be in favor of this conclusion, practical experience will have greater influence. It is fortunate that we can point to actual cases that seem to confirm the logical reasoning. There is in the possession of one of the New York Gas Companies quite a number of different articles of iron and steel that have been unearthed from time to time while excavating for laying gas pipes. Among these are arms and implements that were found in lower New York, and proved to have been originally in the possession of British soldiers. Inasmuch as the British troops sailed away from New York on November 25, 1783, it follows that the articles are now at least 125 years old. While pretty well rusted, these things are by no means entirely destroyed as would be expected. As a matter of fact, it is believed that most of the rusting occurred before the implements were completely embedded, and it is obvious that for some time these articles must have been lying very near the surface, if not altogether exposed.

“I have also seen a piece of gas pipe 2 in. in diameter that was taken up after it has been in the ground for twenty years. This is in such excellent condition that it is impossible to detect any effect of corrosion. The original mill-scale is intact, and, in fact, the appearance of the pipe is such that, except for the thin coating of earthy matter, it has all the appearance of a pipe fresh from the mill. It is the most remarkable evidence of the durability of iron or steel embedded in the ground that I have ever seen.

“At a meeting of the Engineers’ Society of Western Pennsylvania, held recently, during which the question of corrosion was fully discussed, Mr. R. B. Woodworth made the following remarks:

“It may be interesting to state that I have in my possession a piece of iron that was put into the Mississippi River in the year 1863, and that is to-day in as good condition as when it was put in. It was painted with some kind of red paint which looks very much like red oxide of iron, and the paint is just as good

to-day apparently as it was the day it was put in. The conditions there must have been extremely favorable to its preservation. The water of the Mississippi River at that point is probably pure and the iron was buried in the Mississippi River silt, sand or gravel, so as to be protected from exposure to atmospheric conditions, and as a consequence there was nothing to make corrosion.

“I have also a theory that so far as our own rivers are concerned, although they do carry a great deal of free acid, yet when the steel is placed sufficiently below the river-bed as to get the advantage of the filtering action of the sand and gravel, we do not have to do with an acid-laden condition, but rather with the condition of practically pure water free from contact with air, and I think we have every assurance to believe that the life of steel under such circumstances will be indefinite. I was told by the engineers who have charge of the construction of the Black Rock Lock at Buffalo, that the waters of the lake are not considered in any way dangerous, and that steel of ordinary commercial quality in such installations may be expected to last for any reasonable length of time.’

“Further evidence of the durability of iron and steel embedded in the ground is found in the Proceedings of the American Society of Civil Engineers, Nos. 6 and 7, for the year 1907. At the Annual Convention held at Mexico City, July 10, 1907, among various subjects for discussion was the following: Will iron or steel, used in foundations, independently or in combination with other materials, last indefinitely when in direct or indirect contact with water?

“The most interesting contribution to this discussion was, undoubtedly, that submitted by Mr. John F. O’Rourke, the well-known foundation engineer and contractor. Mr. O’Rourke stated that:

“‘Iron and steel used in foundations, apart from conditions where electrolysis may occur, last indefinitely when in direct or indirect contact with water, provided the water remains unchanged. The reason for this is obvious. Water attacks iron or steel, on account of the oxygen it contains, and, if this is a proportionately small quantity, the amount of oxygen contained in wet concrete or ground is negligible, and, having once been exhausted, the metal remains unharmed and protected.

“The writer has seen many cases where immersion in standing water has been a matter of years, and in every case the effect upon the metal has been no greater than if it had stood for the same length of time in linseed oil. In one case bolts on the inside of cast-iron cylinders, filled with concrete, were exposed to the salt water in the Harlem River for more than thirty years, and when removed were found to be without rust. In another case, a pipe was immersed for ten years in an artesian well, the water in which had not been pumped for ten or fifteen years, and no corrosion of this inside pipe had taken place, the scale was still as fresh as when the pipe was new, and the tool-marks of the pipe-coupling apparatus were still perfectly fresh.

“Similar results came under the writer’s observation in reference to the condition of rods and nails found in wood foundations where the surrounding material was impervious to air, and in one case which came under his observation, at the time of the removal of the old elevated railroad columns in Greenwich Street, New York City, prior to making way for the new structure in 1878, the bottom part of these columns and the bolts in the masonry were found intact, the corrosion gradually increasing until near the surface, where the material was almost entirely destroyed by rust. This experience with both wood and iron, where the renewal of the oxygen in the surrounding water was prevented, has been uniformly that of finding the material perfectly preserved, so that, in the writer’s practice, he does not hesitate to advise the use of either material under conditions where a fresh supply of oxygen is excluded.”

“Busy” Iron does not Rust. — We have now to consider the well-known fact that in rapidly moving waters corrosion does not take place so rapidly and dangerously as when the conditions are comparatively quiescent provided dissolved oxygen is present in both cases. This has been a matter of record by pipe-line engineers, who have noted that their dangerous corrosion in buried pipes always takes place from the outside in, and not from the inside, out¹. It follows that if the electrolytic explanation of corrosion is correct, undisturbed and comparatively quiescent conditions are most favorable to the action. Differences of potential establish themselves, as the ferroxy indicator shows, at specific points and nodes. If the conditions are continually

¹ Gaines, *Engineering News*; also Thomson, *Com. Eng.* XLII, 67 (1908).

changing on the surface, it is presumable that the points of potential difference will not be maintained, but, on the contrary, will never remain long enough in one spot to produce deep rusting. It may safely be said that dangerous corrosion is localized electrolytic action. In a pipe-line as in many another case of structural steel, if the corrosion effect was distributed, little damage would accrue, but as a chain is no stronger than its weakest link, so a pipe-line, a boiler tube, or a bridge member can fail and endanger human life only because it has given way at some specific point. One of the authors of this work observed a number of years ago that *busy* iron does not rust, and explained this observation by the fact that frequent and recurrent vibration was sufficient to break up specific points of potential difference on the surface. Sang's observations on this point are interesting in this connection:¹

"The case of steel rails is an interesting one, showing, as it does, the effect of vibration on rusting. A rail which has been in service, but has been laid to one side, will rust all over, but especially at the ends where the vibration of the fish-plates has removed the mill-scale, and on the smooth top of the head. On the other hand, a quite remarkable fact, which has been universally confirmed and can be easily observed by any one, is that a rail while *in service* will not rust nearly as rapidly as one which is lying out of service. The rusting takes place in proportion to the service, and lines over which fast trains pass frequently, causing much vibration, will practically not rust at all, whereas the rails of turnouts or sidings, which undergo less service, and that of a slow nature, will rust to a certain extent. One observer (J. M. Heppel) has reported the case of some rails at Madras, India, which lost three pounds to the yard lying in the yard exposed to the sea air, while the rails in service near by were not perceptibly affected. The top of a rail is compressed and smoothed down in service by the grinding of wheel tires, for there is always a certain amount of slip, especially during acceleration and retardation. Galvanic action between the smooth head of the rail and the rest of it has been suggested to explain this immunity from rust, but it is not at all likely that the foot would owe its protection to the thin stratum of denser metal so far removed from it. If that dense skin on the top of the rail were not crushed

¹ Proc. Eng. Soc. West. Pa., XXIV, 10, p. 523.

beyond its elastic limit, it would, on the contrary, tend to accelerate the corrosion of the steel in contact with it. The real reason for this difference of behavior seems to lie in the observed fact that oxidation is apparently arrested, or at least greatly retarded, by vibration.¹ Explanation seems to stop at this point, but a simple theory can be built on the assumption that the vibration causes a shedding of the rust as soon as it is formed on the spots that are not protected by mill-scale, and there is, therefore, no acceleration of the action due to the accumulation of spongy and electro-negative rust. The average speed of corrosion of a vibrating body would be that of the formation of a first film of rust. Most of the actual rust on rails is probably due to the rapid evaporation of rain on the surface. In the case of rails in service, the first film of rust would be confined to bare spots and cracks in the mill-scale, and the vibration would prevent its working its way under the mill-scale as would happen if the rail were at rest. The top of the rail being denser might be expected to resist corrosion better when the rail is out of use; such is not the case, however. The surface has not only been subjected to hammering and crushing, but also to abrasion and rolling, and it has become short and crackeled and sometimes exfoliated; once laid aside, the smooth top of an old rail rusts very rapidly."

Application of the Electrolytic Theory to Special Corrosion Problems.—There are many applications of the electrolytic theory to special corrosion problems that might be properly included in this chapter. These will, however, be considered separately in the second portion of the book which is specially devoted to the preservation of iron and steel. In addition to this, much of the material given in this chapter might properly be presented in the next chapter, in which the specific bearing of the electrolytic theory on the stimulation and inhibition of corrosion are dealt with. In treating a complex problem of this kind, the arrangement of the material is not a simple matter, but it is hoped that enough has been said to make what follows quite clear to the reader.

¹ Edwin Clark: Proc. Soc. C. E., Yr. 1868, p. 554.

CHAPTER V

THE INHIBITION AND STIMULATION OF CORROSION

Use of the Word "Inhibition." — The word "inhibition" in relation to the corrosion problem was first used by one of the authors,¹ to mean the restriction or repression of corrosion, and not its complete prohibition. As Sang² points out: "The protective effect is, sooner or later, overcome, and clearly indicates that inhibition furnishes *something* to the iron, be it substance or physical state, which under the attacks of corrosive agencies is slowly expended until destroyed or brought below the safe limit of protection." Inhibitory treatments have the effect of rendering iron passive, but the passive condition is not the stable condition, so that there must be a continual tendency at work which causes the return to the normal surface condition. The passive state of the metals has already been described in a previous chapter and it will now be necessary to discuss the subject from the standpoint of the protection of iron.

Hydroxyl Ions as Inhibitors. — All substances in solution which contain hydrogen ions, such as acids, stimulate the corrosion of iron. This is also true of salts of strong acids and weak bases, which, though perfectly stable in a dry condition, hydrolyze in solution to an acid reaction; or which, though neutral in fresh solutions, undergo slow decomposition under the action of light, with the formation of acid salts or free acid. With certain exceptions, salts which are perfectly neutral in solution do not prevent oxidation but appear to aid it by increasing the electrolytic action. All substances which develop hydroxyl ions in solution, such as the alkalis or salts of strong bases with weak acids, to a certain extent inhibit, and, if the concentration is high enough, absolutely prohibit, the rusting of iron.³

¹ Cushman Bull., Office Public Roads, U. S. Dept. Agr. (1907).

² *Loc cit.*, p. 536.

³ Under exceptional conditions this statement may require modification. In this connection see note, p. 100.

Under the electrolytic theory the explanation of the protection afforded by hydroxyl ions is a simple one. Owing to the small dissociation of water, hydrogen ions cannot exist in a solution in which the hydroxyl ions are in excess. As hydrogen ions cannot exist or be locally formed in sufficiently strong alkaline solutions, no attack is made upon the iron, which remains permanently unaltered. If, however, the concentration of the hydroxyl ions is not sufficiently great, electrolysis can go on with an apparent stimulation of the pitting effects similar to that produced by perfectly neutral electrolytes, such as sodium chloride.

Bichromate Solutions as Inhibitors.—As has already been noted, solutions of chromic acid and potassium bichromate inhibit the rusting of iron. In order to determine the concentration necessary to produce complete protection, a number of polished strips of two different samples of steel were immersed in bichromate solutions of increasing concentration, contained in tubes which were left quite open to the air. There were twelve tubes in each series, ranging by regular dilutions from tenth-normal down to ten-thousandth normal. At the end of two months the last four tubes showed graded rusting with accumulation of ferric hydroxide. No rusting had occurred in any of the solutions above tube No. 8, which contained six-hundred-and-fortieth normal bichromate, a strength corresponding to about 8 parts of the salt in 100,000 parts of water, or about 2 pounds to 3,000 gallons. Since solutions of bichromate do not hydrolize with an alkaline reaction, but on the contrary are usually slightly acid, some other explanation must be found for this remarkable phenomenon. On first thought it would seem a paradox that a strong oxidizing agent should have the effect of preventing the oxidation of iron, and yet this is precisely the case. If, however, the initial cause of rusting is the hydrogen ion, it is possible to believe that under certain conditions oxygen would prove the most effective of all inhibitors.¹

Passivity of Chromated Iron.—One of the authors has observed that if a rod or strip of bright iron or steel is immersed for a few hours in a strong (5 to 10 per cent.) solution of potassium bichromate, and is then removed and thoroughly washed, that a certain change has been produced on the surface of the

¹ See explanation of passivity, p. 28.

metal. The surface may be thoroughly washed and wiped with a clean cloth without disturbing this new surface condition. No visible change has been effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water it will be found that rusting is inhibited. An ordinary untreated polished specimen of steel will show rusting in a few minutes when immersed in the ordinary distilled water of the laboratory. Chromated specimens will stand immersion for varying lengths of time before rust appears, but the induced passivity gradually disappears.

The passivity which iron has acquired can be much more strikingly shown, however, than by the rusting effect produced by air and water. If a piece of polished steel is dipped into a 1 per cent. solution of copper sulphate, a 10-second immersion is sufficient to plate it with a distinctly visible coating of copper which cannot be wiped off.¹ A similar polished strip of steel which has been soaked over night in a concentrated solution of bichromate and subsequently well washed and wiped will stand from six to ten 10-second immersions in 1 per cent. copper sulphate before a permanent coating of copper is deposited. Even a momentary plunging of the metal into the bichromate will induce a certain passivity, but the maximum effect appears to require a more prolonged contact with the solution.

Bichromate Solutions do not Attack Iron Free from Manganese. — Moody² asserts that potassium bichromate prevents the formation of rust, owing to the fact that it slowly dissolves iron and its hydroxides. He observed that the addition of ammonia to solutions of chromic acid and its salts which had been allowed to act on iron produced precipitates of hydroxide. This point has been carefully investigated by the authors, with the following results: Iron which is free from manganese is not attacked by solutions of bichromate, even if boiled for days in a flask fitted with a return condenser. Manganese is, however, readily soluble in bichromate solutions, and therefore iron rich in manganese yields a sufficient amount to the solvent action to produce a small amount of brownish manganese hydroxide when the bichromate solution is poured off, made slightly ammoniacal, and

¹ This experiment has failed in hands of certain experimenters who have not been careful to use the copper sulphate solution as dilute as directed.

² Proc. Chem. Soc. (Lond.), 1906, 22, 15.

allowed to stand. If metallic manganese is boiled in bichromate solutions it dissolves readily, and subsequent addition of ammonia produces an abundant precipitate of brown manganese hydroxide.

Experiment with Bichromate to Induce Passivity. — In order to show beyond doubt that a passive condition is induced by immersing iron in a strong solution of bichromate the following experiment was made: Two polished steel electrodes were prepared and chromated by immersion for a number of hours in a strong solution of potassium bichromate. The prepared electrodes were then thrust tightly through a rubber stopper which closed the Jena flask A, which was then filled with pure freshly boiled distilled water in the manner shown in Fig. 7. The electrodes were then attached to the poles of a primary battery at about two volts potential. At the end of half an hour although the potential was not sufficient to disengage bubbles of gas and no visible change had occurred, the electrode which was connected to the zinc pole of the battery had lost its passivity, the other retaining it.

Inhibitive Power of Pigments Containing Certain Oxidizing Agents. — Wood¹ in 1895 commented on the power of paints and pigments containing certain oxidizing agents, notably potassium bichromate and lead chromate, to form on iron and steel surfaces a thin coating of oxide which so effectually protects the metallic surfaces from corrosion that after the removal of the paint the metal still resists atmospheric effects for a long time, as well as the stronger effect of immersion in sea-water or acidulated waters and sulphurous and other vapors. This action, Wood adds, is very obscure and not thoroughly understood; but the fact remains, and extended experiments in this field only demonstrate its presence and usefulness.

Solution System with Two Contending Forces, Inhibitive and Stimulative. — It has been already pointed out in a previous chapter that in many cases a stimulative and an inhibitive tendency may be at work at one and the same time. This assertion is well brought out by the following experiment in which an inhibitor and stimulator are literally "pitted" against one another. Samples of bright steel wire were immersed in 100 cubic centimeters of a very dilute one-thousandth normal solution of potassium bichromate in a series of shallow dishes. The wire-

¹ Am. Soc. Mech. Eng. Trans., 1895, 16, 671.

test pieces were suspended in the solution so that they did not come in direct contact with the glass surfaces of the dishes. This precaution should never be omitted in experiments of this kind, as owing to the absorption of air by glass, rusting is always stimulated at the point of contact between glass and iron. The first dish was left as a blank, the second received one drop equal to $\frac{1}{10}$ cubic centimeter of a dilute tenth-normal copper sulphate solution. The third dish received two drops of the solution, and so on, each dish getting an increased amount of copper sulphate until twenty-five dishes had been prepared.

Now it is apparent that we have in this system two contending forces at work. Iron has a higher solution tension than copper, and therefore tends to pass into solution, the copper tending to plate out on the iron. Chromate ions, on the other hand, put the surface of iron in a condition in which it cannot pass into solution. In the solution system iron-chromate-copper we have an equilibrium to be decided between two contending forces acting in opposite directions. It was interesting and instructive to note the results of this struggle, which was known to be going on, although the actual conflict could not be watched. In the first dish, in which no copper was present, no corrosion took place; in the second, also, no action was visible; in the third, however, minute specks of iron rust appeared. These were larger and more frequent in the immediately succeeding dishes, the test-pieces showing rust tuberculation with the well-known pitting effect. As the middle of the series of dishes was approached, both iron rust and precipitated copper began to appear side by side on the surface of the iron, and from thereon in the series more and more copper separated, while less and less rust formed, until in the end dishes copper and iron were changing places evenly over the surface without apparent hindrance. These experiments, and others of a similar nature, were repeated many times with the same results, and there seems to be no escape from at least the following two conclusions to which they obviously lead:

- (1) If the surface of iron is subject to the action of two contending influences, one tending to stimulate corrosion and the other to inhibit it, the result will be a breaking down of the defensive action of the inhibitor at the weakest points, thus localizing the action and leading to pitting effects.

(2) While the concentration of an inhibitor may be strong enough to prevent the electrolytic exchange between atom and ion, it must be still stronger to prevent entirely the solution of iron and the subsequent oxidation which leads to the formation of rust-spots.

Practical Bearing of Alkaline Solutions on Corrosion.—In the opinion of the authors these observations have a direct bearing on, if they do not actually explain, many of the practical problems of corrosion. It is well known that if sufficiently alkaline, solutions inhibit and in some cases actually prohibit corrosion. If the concentration of the hydroxyl ions is not sufficiently high, however, local electrolysis goes on in the slightly alkaline medium and the tendency to pit is actually stimulated, as was noted by Cribb¹ in an extended investigation. Pennock² has shown that concentrated ammonia solutions not only do not rust clean iron but prevent its rusting in the presence of corrosive agents, and yet dilute ammoniacal liquors appear to stimulate corrosion. It is a curious fact, however, that iron is to some extent soluble in strong boiling solution of ammonia, although there is no apparent action in the cold. This phenomenon is now being investigated.

One of the authors has suggested that pipe lines trenched with lime or limed soil should be to some extent protected, but it is still a question whether or not the tendency to pit would not be stimulated. Knudson³ has called attention to an interesting case of the stimulated corrosion of the bottom of oil tanks. In the process of purifying oils it is customary to treat them with sulphuric acid and after washing to neutralize the residual acid with a slight excess of caustic soda. The slightly alkaline liquors containing sodic sulphate which remain and settle to the bottom naturally stimulate corrosion to a very high degree. The natural cure for this difficulty which suggests itself would be in increasing the alkalinity of the oil lees until the prohibition point was reached. It might also be possible to use an excess of potassium bichromate for this purpose, provided it was found that this oxidizing agent did not react with the oil.

¹ Analyst, 30, 225, also Engineering, 81, 32.

² Jour. Am. Chem. Soc., 24, 377.

³ Trans. Am. Electro-chem. Soc., XIV, 189 (1908).

Stimulative Action of Certain Paint Films Acting as Depolarizers. — Walker¹ has shown that the effort to protect the interior of tinned cans by the application of a lacquer made from a high-grade copal linseed oil varnish only led to stimulated corrosion in the form of pit holes. This unexpected result Walker was enabled to explain satisfactorily by means of the electrolytic theory. It appears that the varnish acted as a depolarizer by absorption of hydrogen, and therefore at every scratch or imperfection in the lacquer a stimulated pitting effect was operative. Walker, at the suggestion of one of the authors, has also applied this same reasoning to the general subject of protective paint coatings, with interesting results. Walker's method of investigation and conclusions are quoted in the following paragraphs:

"To show that the corrosion of the iron occasioned by the lacquer film is accompanied by the flow of an electric current through the external circuit, the following experiment was tried: A U-tube with a KCl solution and an agar plug, carefully boiled out, the whole under an atmosphere of hydrogen, contained two iron electrodes, the one bare and the other covered with a linexylin film. An electrometer was inserted into the external circuit and the current flow measured as shown in the table below. It was found undesirable to use a silver voltameter for the excessively small currents employed and resort was had to a modification of Ostwald's Bromide Voltameter. This voltameter was used for all measurements made, after the first, which was done with the silver nitrate instrument.

"Deposit obtained from current due to depolarization by two different linexylin films:

	Time in Hours	Deposit of Mgs. Bromine	Deposit Mgs. per Hour
Film No. 1.....	48	0.6	0.012
	76	1.0	0.013
Film No. 2.....	41	1.8	0.044
	89	4.1	0.046
	185	8.7	0.047

"These figures prove beyond doubt that the corrosion of the iron on the unlacquered side is due to the flow of an electric current through the external circuit from the lacquered surface.

¹ Jour. Ind. and Eng. Chem., I, II, 754.

"These experimental facts seem to allow of but one explanation, namely, that the films in question are porous in their nature, allowing the electrolyte to penetrate them to the surface of the metal beneath, that some of these films, due to their unsaturated state, are capable of absorbing nascent hydrogen and in this way acting as depolarizers, and that aside from this, all the porous films allow the penetration through them to the surface beneath of any depolarizer that may exist in the solution, thus rendering the coated surface cathodic and concentrating the solvent action at the exposed part of the metal.

"The reason for the failure of the fruit cans mentioned at the beginning of this article is now easily understood. While the lacquer film applied to the uncut sheet was probably a perfect one, still, in the process of making the can, this film was ruptured at many points. Thus the die stamping out the head of the can broke the film at the place where the tin was bent; the mandrel, on which the body of the can was formed, scratched the sides in long parallel lines upon the removal of the can, and the burning of the joints destroyed the lacquer in their immediate neighborhood. When the fruit was introduced into the can, the depolarizing action of the lacquer itself, coupled with that of the small amount of air left in the can in packing, threw the protected areas into the cathodic state, concentrating the solution of the metal at the exposed points, dissolving in this way both tin and iron, and maintaining this corrosion until both the air was consumed and the unsaturated state of the lacquer was completely relieved. Before this point was reached, however, the corrosion had gone far enough to seriously damage the fruit and even in many cases to puncture the can. This action is entirely independent of any possible imperfections in the tin plate. The remedy would be to find a lacquer impervious to the solution, or if that prove impracticable to at least furnish one which will not act as a hydrogen depolarizer. A non-porous lacquer it has as yet proven impossible to find; a saturated one can be made by sufficiently baking any ordinary varnish, but there still remains work to be done to develop this into a satisfactory solution of the problem.

"It is self-evident, however, that the importance of these phenomena is by no means limited to the problem of lacquering fruit cans. The majority of protective coatings for iron contain linseed oil or some one of the various substances found by our

experiments to be either unsaturated, or porous, or both; and so soon as a piece of metal painted with these substances comes in contact with water after the abrasion of the paint film at any point, all the conditions for corrosion as above outlined are fulfilled, and we may be sure that corrosion at the exposed point will be accelerated by the presence of such films in its neighborhood. It is true that the porosity of these films is reduced to a minimum by the use of the best obtainable loading materials, such for instance as certain pigments of ordinary linseed paints, the bituminous bodies of asphalt or coal tar paints, etc., and that these paints offer in consequence a much greater electrical resistance to the flow of the current than otherwise. One must not forget, however, that the insertion of such a resistance to the current flow can only reduce the rate of the reaction, and in no way influence its tendency or driving force. The exposure of such films to the air for a long period of time finally entirely saturates them, but this again does not affect their porosity and consequently does not preclude the possibility of acceleration of corrosion at the exposed point due to the depolarizing action of air through the film. These facts make clear the reason for the rapid deterioration and pitting of the iron or steel surface at points laid bare by the breaking down of many paint films, and show why it is so exceedingly important that a metal surface should be clean and bright before the application of a paint.

"If a paint or lacquer film be intact, despite the fact of its porosity, corrosion does not seem to take place at once beneath its surface. Thus an iron can, carefully painted with a high-grade varnish and filled with cold 5 per cent. sulphuric acid, showed a test for iron with ferricyanide first after twenty-four hours. If heated on the water bath, however, a test could be obtained in slightly over one hour, but even then the action was not severe. It may perhaps be that the electrolyte does not find sufficient continuous surface beneath the film to allow of a ready separation into cathodic and anodic areas. At any rate, corrosion does not readily take place if the film be intact, but the surface below the film does easily become cathodic if an exposed area in the neighborhood can act as an anode. This cathodic liberation of hydrogen loosens the film from the metal in some way not yet clearly understood and likewise softens it. The resistance of a film diminishes quite rapidly in this way, and it

soon becomes weak and rotten and easily removable from the iron. It is easy to see how, especially with rough usage, exposed points in a painted steel surface rapidly grow in size.

A few of the common commercial paints and paint-making materials were examined, using the following apparatus: A glass U-tube of one inch tubing with six inch arms and eight inches in length over all, contains 200 c.c. of normal KCl. The electrodes are of commercial soft iron wire, 0.044' diameter, carefully cleaned with emery. The bare electrode is 25 cm. long and the lacquered one 100 cm. The electrode is coated by dipping in the paint to be examined, the excess removed by rapid twirling and then dried. The water about the *cathode* is kept saturated with oxygen by bubbling air through it. The depolarization current is measured by the use of the bromide voltameter already mentioned. The bromide deposited is proportional to the time, up to a point when the film gives way. This point of disintegration is different for different films and two quantities can in general be measured, (1) the initial rate of depolarization and (2) the time of rupture.

Paint film	Corrosion in mgs.	- Bromide per hour.
"Durable metal coating"		0.70
"Copal linseed oil lacquer"		0.76
"Cosmos" (coal tar)		0.34
Graphite		1.87
Carbon black		2.4
Lampblack		2.3
Zinc chromate		0.11 ¹
Barytes		1.2
Zinc oxide		0.078 ²
Graphite (baked)		0.078
White lead		0.10 ³
Linoxylin		0.31
Paraffine		0.00

"This second factor is somewhat difficult to obtain because our voltameter measures not current but total amount of electricity passed, and it is frequently, if not usually, impossible to tell at exactly what point the increase in current began. In the above table is the average of the data obtained. It is evident that the electricity measured by the bromine deposited is the resultant

¹ Broke down in 36 hours, but not badly.

² Still perfect after 71 hours.

³ Broke down in 30 hours.

of a number of factors acting at the same time. A comprehensive study of the relationship between such data and the value of various paints as a protective coating for iron is now in progress."

It is interesting to note at this place, that this work furnishes a striking corroboration of the stimulative and inhibitive effects of certain pigments which had already been indicated by one of the authors, in a series of preliminary tests carried out on the inhibitive power of certain pigments. This work will be presented in detail in a later chapter.

Wounds on Steel Surface Stimulate Rusting. — A considerable body of evidence has been brought forward from time to time to show that in addition to the segregation of impurities in steel, the presence of scratches, sand pitholes, and, in fact, all indentations or wounds on the surface of steel, will stimulate rusting by becoming centers of corrosion.¹ Such marks or indentations are almost invariably electro-positive to surrounding areas, and the depolarization which results in the rapid disengagement of hydrogen at these spots leads to stimulated pitting. This effect can be very prettily shown by means of the ferroxyl indicator. In the illustration shown in Fig. 31 a freshly polished steel plate has had the word "Rust" carved upon its surface with a cutting tool. On immersion in the ferroxyl indicator the general surface has come out in red while the carved letters appeared in blue. This cause of stimulated pitting is probably very generally active on all surfaces of iron and steel which from the nature of their service cannot be treated with any form of protective coating. Boiler tubes furnish the best example of stimulated corrosion effects from this cause. The remedy should lie in truing up of all active contact surfaces even to the point of polishing if necessary. There are times when a sound boiler tube is of vastly more importance than a polished gun barrel, and when the added cost of preparing the boiler tubes would be insignificant in comparison with the danger of blow-outs from pitting. The above fact brought out by experimental investigation is also attested by the results of practical observation and experience. It has long been known in the Bureau of Steam Engineering of the U. S. Navy Department² that indentations such as sandpits, or injuries on the water surfaces of boilers, always become centers of corrosion

¹Cushman, Proc. Am. Soc. Testing Materials, VIII, 605 (1908).

²Proc. Am. Soc. Testing Materials, VIII, 244 (1908).

and pitting, and inspection has been as thorough as possible to guard against this danger.

Mill-scale a Stimulator. — It has already been shown in a previous chapter that mill-scale consisting of the black magnetic oxide of iron is electro-negative to the metal, and this acts inevitably as a common cause of stimulation of corrosion, whenever the coating of mill-scale is discontinuous on the surface. This point is now so well and generally understood that pickling and sand-blasting are often resorted to in order to obtain clean surfaces of metal, before protective coatings are applied.

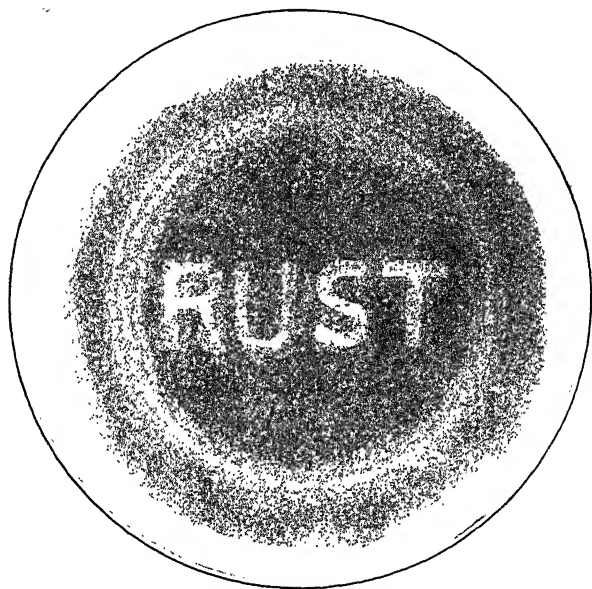


FIG. 31. — Showing the effect produced in the ferroxyl indicator by cutting the surface of a polished steel plate. (Cushman.)

Various Inhibitive Expedients which have been Tried. — Almost all efforts to inhibit the corrosion of iron depend either upon producing and maintaining a passive condition of the surface or on maintaining a sufficiently alkaline medium in contact with the surface of the metal. Chromic acid and its more or less soluble salt furnish the principal chemical means of producing passivity. It has long been known that, if iron is made the anode in an electrolytic circuit, it will not rust, provided the quantity of current

passing is sufficient to protect it. Various expedients based on this fact have been suggested or tried in order to inhibit corrosion. Among these should be mentioned the insertion of zincs in boilers, and the use of zinc-corroding plates in connection with steel structures. Zinc, as has been shown, is electro-positive to iron, and when the two metals are in contact and wet with a corroding medium zinc will pass into solution and the iron will be protected. The sphere of influence of the zinc does not, however, extend far from the point of contact between the two metals



FIG. 32. — Illustrating the protection on the surface of the steel in the immediate neighborhood of a button of zinc soldered into the steel. The sphere of influence of the zinc is shown to be proscribed. (Cushman.)

so that iron can begin to rust in places long before all the zinc is destroyed. This can easily be shown by soldering a button of zinc into the machined surface of a plate of steel and immersing the whole either in water or in the ferroxy indicator. This is very well shown in Fig. 32. In general it may be said that even if the sphere of influence of the zinc was wider, the idea of burning up zinc in order to protect steel does not commend itself.

Passivity Maintained by Plunging Electrodes into Neutral or Alkaline Solution. — If two iron electrodes are plunged into a

neutral or alkaline solution and an electric current of sufficient density be passed through the circuit the pole where the oxygen disengages becomes passive, and while it is maintained in this condition rusting is inhibited or actually prohibited. Just as in the case of passivity induced by solutions of chromic acid and its salts, this passive condition is maintained to some extent after the removal of the cathode plate from the circuit. This action has been studied by a number of experimenters including the authors. Toch¹ has made a very recent contribution to the subject, the details of which are not yet available.

Rusting Caused by Escaped Currents.—It is very generally known that extraneous escaped currents from high-potential light and power circuits do great damage to structural iron and water mains, especially in the larger cities. There is a vast literature on this subject, much of which is cited in Appendix B. No effort will be made here to abstract the available information, as this phase of the subject constitutes a special problem on which a separate volume might be written. In a general way it may be stated that the best preventive measures against this cause of rust stimulation are more judicious bonding of the rails carrying return currents and the use of effective feeders on the electric circuits, the maintenance of a negative condition of the structural material or pipe lines, or their more thorough isolation and insulation. For more detailed information on this phase of the subject the original literature should be referred to.

Factors Causing Stimulation or Inhibition.—The effort has been made in this brief chapter to set forth the principal factors which enter into the stimulation or inhibition of corrosion. Some of these factors, such as contact action in the air and in water, had already been treated in previous chapters, but may be conveniently summarized here in the following list:

FACTORS WHICH STIMULATE CORROSION

- (1) Impure and segregated metal. Unhomogeneous or burnt metal which may contain blow-holes.
- (2) Cold rolled or improperly annealed metal which may maintain an uneven, stressed, or strained condition.
- (3) Contact action, in which different types of iron and steel are used in one and the same structure.

¹ Proc. Am. Electro-chem. Soc. (1909).

(4) The presence of hydrogen ions from any source whatsoever that may be brought in contact with the surface, in water or other electrolytes in the presence of oxygen.

(5) The concentration of active oxygen that is present in the wetting medium.

(6) The presence of electrolytes generally in the wetting medium. Even hydroxyl ions and other inhibitors may appear as stimulators if in insufficient concentration.

(7) The stimulating or depolarizing effects of certain coatings applied to iron and steel with the object of protecting the metal.

(8) The effect of indentations, scratches or other injuries which become centers of corrosion.

(9) The effect of extraneous or stray currents escaped from high-potential circuits.

FACTORS WHICH INHIBIT CORROSION

(1) In most cases the reverse of the conditions which stimulate corrosion.

(2) Contact with certain substances in solution, such as chromic acid and its soluble salts which produce a passive condition.

(3) Alkaline solutions of all kinds in which the concentration of hydroxyl ions is sufficiently high. But this protection may be overcome and the equilibrium conditions reversed in very strong boiling alkaline solutions.

(4) Contact with more electro-positive metals.

(5) Electrolysis under certain specific conditions.

CHAPTER VI

THE TECHNICAL PROTECTION OF IRON AND STEEL

The Different Phases of the Protection Problem.—No purely scientific discussion of the corrosion problem will be considered complete unless it also describes the more recent efforts to attain efficient protection of the numerous forms of iron and steel which enter into common use. This phase of the problem may be conveniently considered under three main heads: (1) Protective coatings of other metals and alloys. (2) Magnetic oxide surfaces. (3) Paint coatings, including linseed oil paints, varnishes, lacquers, bitumens, and cements.

The protection of iron is presumably a problem which in the ease of its solution varies directly with the rust-resisting character of the metal to be preserved. Progress in the manufacture of more rust-resistant metal must keep pace with an added efficiency in the methods of protection. That there is much still to be accomplished along both these lines is attested, not only by the complaints of innumerable consumers, but also by the records of the proceedings of engineering and other learned bodies and by the technical and scientific press.

Metallurgists are exhibiting a growing tendency to look upon the structure of iron and steel as an aggregate in the same sense that geologists consider crystalline rock structures to have resulted from the more or less gradual cooling of molten magmas. From this point of view, careful study and control of the heat treatments which steel receives in the course of its manufacture is of the utmost importance if constancy of chemical constitution and physical character is to be developed. Upon just such factors as these resistance to corrosion will be found dependent. The mill man's purposes are often expedited by turning a stream of cold water upon red-hot piles of freshly shaped forms. How many mill men, however, have ever given consideration to the structural changes produced in the metal by such sudden quench-

ing? Even subsequent annealing unless properly done will not restore the original homogeneous and quiescent conditions in the structure of the steel as the classic researches of Heyn and Bauer previously quoted very clearly show. The authors would earnestly recommend to manufacturers who desire to produce rust-resistant iron, that every step in the heat treatment which the metal receives from the furnace to the finished shape be studied with reference to its possible effect upon the final product.

One way to attain homogeneity in the metal is to eliminate all the impurities and thus produce a practically pure iron. This has to a very considerable extent been accomplished on a commercial scale within the last few years, and metal of this type is now on the market. Every metallurgist knows that steel which is free from manganese is difficult to roll, and that special care is necessary in order to shape it successfully. Even if the influence of manganese as one of the many factors which control resistance to corrosion is denied, it is none the less probable that a metal which from its very nature must receive careful and even heat treatment, will be more resistant than one which will permit itself to be carelessly and rapidly pushed through the mill.

Until the last few years, the methods of protection have been carried out mainly on an empirical basis. When iron had been coated with any substance which was believed to furnish a fairly good and durable waterproof surface it was considered that nothing more could be done. Of course, serious efforts were made to improve the physical character of the coatings as to their water or acid resisting qualities, but little or no attention was paid to the possible electrolytic effects produced, for indeed the fundamental causes of corrosion were not understood. For this reason many of the so-called protective coatings were actually stimulating the very kind of corrosion that they were designed to prevent.

Protection with Zinc. — In any discussions of the use of other metals for the protection of iron, zinc must take the front rank. Zinc is the most electro-positive metal which can be practically used for coating iron and is from this point of view better suited for the purpose of providing an inhibitive coating than any other. On the other hand the solution tension of zinc is high¹ and its power of protecting iron is accomplished mainly at the expense

¹ Davies, Jour. Soc. Chem. Ind., 18, 102.

of its own destruction. For this reason zinc must be considered at the very best as an inhibitor rather than as a prohibitor of corrosion, and the day must inevitably arrive when even the best of zinc coatings will fail. There is reason to believe, however, that the last word on the protection by zinc has not been spoken and that the methods of galvanizing may be so improved as to lengthen the life of the coatings by many years. It is probable that more than half of all the zinc produced is used for the purpose of protecting iron and steel. Burgess¹ has well said that the efficiency of the zinc coating varies greatly with the purity of the metal, its thickness, continuity, and methods of application, though the degree to which these various factors affect the efficiency seems to have received little attention, if one may judge by published data. As a matter of fact the electrolytic theory of corrosion has opened up a number of questions which bear directly upon the efficiency of zinc coatings, and the answers to which, when they are available, will constitute new and valuable data on the subject. These points will be brought out in the following discussion.

Methods of Applying Zinc Coatings. — There are only three processes in general use for coating iron with zinc, although the methods of application under the three processes may vary to a considerable extent in practice. These methods are well known as the hot dip, the "cold" or electrolytic, and the vapor or Sherardizing processes. It is not necessary here to give a detailed account of the technology of these several methods, as it is assumed that the reader is either already familiar with the main and well-known details of the technology of zinc coating or can easily become so by referring to any standard work on the metallurgy of iron and steel. The principal effort that will be made here will be to apply the most recent theories and results of investigation to the problem of securing greater longevity for the protected iron. An examination of the literature of the subject as given in Appendix B will reveal the fact that many claims and counter claims have been put forward and vigorously defended in the effort to show that one or other of the processes is the more efficient or superior. Thus one author² states: "The zinc applied by the hot method usually contains lead, tin and iron. It has

¹ Electro-chem. and Met. Ind., III, 1, 17 (1905).

² Cowper-Coles, quoted by Burgess, *loc. cit.*

been found that iron above 3 per cent. makes the zinc too brittle to bend. Lead up to 1 per cent. is harmless, but above 1.5 per cent. will not dissolve and the excess collects (segregates) and forms weak spots. On the other hand zinc applied by the electric process is very pure and it is found to resist the corroding action of a solution of copper sulphate very much better than hot galvanized iron."

This statement indeed brings out some of the disadvantages of the hot-dip process, although by no means all of them; on the other hand, it does not refer to those which argue against the cold process. As a matter of fact it is probably true of the three methods of applying zinc that each will find its special field of usefulness, and that each will be found to have certain advantages and disadvantages. Further than this, it is quite certain that all the processes are at the present time more or less imperfect and are therefore subject to improvement as time goes on. These processes will now be criticised from the standpoint of the electrolytic theory as it applies to the corrosion and preservation of iron and steel.

The Hot-dip Method of Galvanizing. — In the hot-dip method the iron to be galvanized is dipped or drawn through a molten bath of spelter, which necessarily becomes more and more alloyed with iron up to the point where a definite eutectic alloy of iron and zinc crystallizes out, and being heavier than the molten magma falls to the bottom of the bath. This separated alloy is technically known as dross and is occasionally raked out of the bath and thus partially removed. The layer of partly oxidized zinc and impurities which forms on top of the bath is scum, and this also is removed from time to time. It will be seen that even if the original spelter was pure zinc, it would not remain so in the bath, as it would soon become contaminated by the iron which is immersed in it as well as by other impurities which might accidentally find their way in. As a matter of fact, however, the original spelter contains a certain amount of impurity in the form of lead, cadmium, iron, and other materials, and is therefore really an alloy to begin with. Burgess¹ truly remarks on this subject: "Such an alloy will dissolve very readily in an acid solution, owing to local action, which is set up between the different metals. This results in a more rapid corrosion than where a single metal

¹ *Loc. cit.*

is immersed in a corroding solution." In other words, all that has been said in previous chapters in regard to the accelerated corrosion of impure and segregated iron applies equally to zinc. Not only is the solution tension of zinc alloyed with iron and other impurities greater than that of pure zinc, but even its electrochemical relation to iron is said to change so that it may appear electro-negative instead of electro-positive. These facts will always operate against the efficiency of zinc coatings applied by the hot-dip process, but nevertheless, with proper care, improvement in the results obtained should still be attainable. It is common practice in the hot-dip process to pass the iron or steel to be coated through a hydrochloric acid fluxing bath just before it enters the spelter bath. In many cases zinc chloride or ammonium chloride, "sal ammoniac," is used in conjunction with hydrochloric acid. Certainly no more corrosive mixture than this could be applied to the surface of iron, and it is equally certain that small portions of these acid products become included in the zinc coatings. One of the authors has dissolved a number of samples of hot-dip galvanized coatings in pure dilute nitric acid and never failed to get slight white precipitates with silver nitrate, proving the presence of chlorine ions. In some of the foreign practice much more attention is given to the control of the acidity of the fluxing bath than is usual in this country, and this fact undoubtedly is contributory to higher rust-resistant qualities. For this reason the authors have suggested the substitution of alkaline fluxing and soldering solutions. Adopting the suggestion, experiments have been carried out in a prominent wire mill, on the use of a flux made by dissolving zinc oxide in a fairly strong solution of caustic soda. No trouble was experienced in getting heavy coatings of zinc on the wire with this flux, but occasional black spots appeared which interfered with the general efficiency of the coating and which have not as yet been explained. It is therefore not now certain whether a practical substitute for the acid flux can be found.

All galvanized wire manufacturers have been to some extent troubled by the appearance on their finished products of a whitish efflorescence which often appears in little spots on the surface and which is technically spoken of as "mold." This appearance is undoubtedly due to zinc oxide which, formed as the result of electrolysis, marks a preliminary step to the final failure of the

coating. The fact that chlorides included between the iron and the zinc will stimulate such an effect even if it is not the sole cause cannot be contested. The system $\text{Fe} - \text{FeCl}_2 - \text{ZnCl}_2 - \text{Zn}$ is a galvanic couple which, however well it may justify the name of "galvanized" iron, would certainly tend to hasten corrosion. If a practical galvanizing pan could be devised in which the zinc was melted and maintained in a molten condition out of contact with the air or in an atmosphere of inert gas, better results would be obtained. The excessive amount of scum which forms on top of the spelter bath dirties the coating and prevents the formation of an even and homogeneous layer of zinc.

The Weight of the Zinc Coating. — In addition to the purity, density, and homogeneity of the zinc coating, insufficient thickness is also a contributory cause of rapid corrosion, especially in the case of galvanized wire. Thin coatings of zinc are to some extent porous, a condition which leads naturally to electrolytic destruction of the zinc. By increasing the thickness of the coating the pores are gradually filled up so that less opportunity exists for centers of corrosion to form. The method which is in most general use for determining the thickness of a zinc coating is the well-known copper sulphate test. The test depends upon the fact that if zinc is dipped into a strong solution of a copper salt it goes into solution and copper comes out. As soon as the zinc is removed from the iron the copper begins to plate out slowly on the iron and can be easily seen. The difference of solution pressure is much greater as between zinc and copper than as between iron and copper. The consequence of this is that copper replaces the zinc so rapidly that it makes a crumbly deposit easily wiped off. The copper iron exchange on the other hand takes place so slowly that the copper plates on the surface of the iron so that it cannot be wiped. The appearance of copper plate is therefore an indication that the zinc is gone.

The Preece or Copper Sulphate Dip Test. — This test which is known as the Preece Test is only an approximate method for determining the thickness of a zinc coating and cannot be interpreted as a measure of the life of the coating or its resistance to corrosion under the conditions of service. A difficulty in carrying out the test has been found because there is no sharp point in the reaction which indicates the exact point when all the zinc is gone.

This point is defined by the Chief Engineer of the Western

Electric Company as follows: "The standard color of a bright metallic copper deposit on a sample will be defined as the one obtained by taking a piece of the same class of sample and immersing in hydrochloric acid until the action ceases, after which the sample is immediately washed and wiped dry, and immersed in the standard copper sulphate solution for not over a minute, then removed, washed, and wiped dry. The copper deposit thus obtained will be the bright metallic copper deposit referred to in the specification. These standards should be made every test day. The specific gravity of the standard solution will be determined by a standard 6-inch hydrometer with only one mark on the scale which indicates 1.186 specific gravity at 65° F. In reading these hydrometers the following must be observed: (a) Clean and dry hydrometer before placing in standard solution. (b) Depress the hydrometer so that the solution wets the tube at least $\frac{1}{4}$ in. above the 1.186 mark. (c) Sight just under level of solution to see if the 1.186 mark is on the solution level outside of the capillary."

The American Steel and Wire Company have adopted the following instructions for carrying out the copper sulphate test, which has been found useful in maintaining a standard weight of zinc coating on wire:

Standard Solution. — The standard solution of copper sulphate shall consist of commercial copper sulphate crystals dissolved in cold water about in the proportion of 36 parts by weight of crystals to 100 parts by weight of water. The solution shall be neutralized by addition of an excess of chemically pure cupric oxide (CuO). The presence of an excess of cupric oxide will be shown by a sediment of this reagent at the bottom of the containing vessel. The neutralized solution should be filtered before using. This solution shall have a specific gravity of 1.186 at 65° F.

Small differences in the density of the solution may be corrected by adding water or copper sulphate crystals according as the solution is too heavy or too light, but if the solution is not nearly correct or has become dirty or impaired for any reason it must be thrown out and a fresh supply obtained.

Cleaning of Samples. — Samples must be cleansed thoroughly of oil and dirt by dipping in benzine or gasoline, then thoroughly rinsing in clean water and wiping dry with clean white cotton waste before making the test.

Apparatus. — The apparatus required for the test is as follows:

1 Fahrenheit thermometer with large scale to read up to at least 80° F.

1 Specific gravity hydrometer.

1 Hydrometer cylinder 3 in. by 15 in.

2 Jars for washing samples.

4 Glass test jars 2 in. in diameter and 5 in. in height.

1 Copper or galvanized sheet steel box equipped with running water and waste pipe connection and with a rack for holding thermometer and a tray over part of the box through which test jars may be immersed in the water to maintain constant temperature. White cotton waste free from grease. Benzine or gasoline.

The place for testing should be clean and with good natural light. A cupboard should be provided for the apparatus in which it can be placed when not in use and there should be both hot and cold running water connections. For tests in summer time ice may sometimes be required, but this should seldom be necessary as the cold water supply is nearly always lower than the testing temperature.

Test. — Fill one of the glass test jars with standard solution to a mark one inch from the top. The temperature of the solution must not be lower than 65° nor higher than 70° F. at any time during the test, and the water used for washing samples must be the same.

Not more than seven wires shall be simultaneously immersed in one jar, and they must be grouped together but must be well separated so as to permit the action of the solution to be uniform on all immersed portions of the samples. The ends outside of the solution must not be grouped together. The ends inside jar are likely to touch, but this is not objected to, as indications on the lower inch of the samples are disregarded, as stated below. After each complete test of seven wires or less the solution must be thrown away and fresh solution taken for the next set.

The specified dip must be made on each sample and the periods of time accurately observed. After each dip the samples must be immediately rinsed in water having a temperature within the specified limits of the solution temperature, thoroughly cleaned with soft cotton waste (not with a brush) and wiped dry. Samples must be dry at the time of immersion. For an extended series of tests the wash water should be frequently renewed, for obvious

reasons, and in order to maintain the proper temperature of the wash water the jars should be placed in the same tray as the test jars.

Specified Dips. — The standard method of making a test is as follows, using a “two-minute” immersion test for the purpose of illustration:

The cleansed, washed and dried samples are immersed in fresh standard solution, within the temperature limits of 65° to 70° F., for exactly one minute. They are then removed, rinsed in water, of the proper temperature, and wiped with cotton waste so as to remove the dark deposit which forms, and until they are dry. They are then immersed again in the same solution for exactly one minute, removed, rinsed and wiped as above. Samples so treated should show no trace of metallic copper on the steel more than one inch from the end, although they may be black, indicating nearly complete removal of zinc. If they do show copper on the steel they will be considered to have failed on the test and will be so marked in the record book. Occasionally copper deposits on the zinc, without removing the latter, and can be scratched off without destroying the zinc coating. Such cases, after the second immersion, are not counted as failures.

The engineering department of the American Telephone and Telegraph Company have adopted the following test specifications for galvanized iron and steel wire:

These specifications give in detail the test to be applied to galvanized material. All specimens shall be capable of withstanding these tests.

(a) *Coating.* — The galvanizing shall consist of a continuous coating of pure zinc of uniform thickness, and so applied that it adheres firmly to the surface of the iron and steel. The finished product shall be smooth.

(b) *Cleaning.* — The samples shall be cleaned before testing, first with carbona, benzine or turpentine, and cotton waste (not with a brush), and then thoroughly rinsed in clean water and wiped dry with clean cotton waste.

The samples shall be clean and dry before each immersion in the solution.

(c) *Solution.* — The standard solution of copper sulphate shall consist of commercial copper sulphate crystals dissolved in cold water, about in the proportion of 36 parts, by weight, of crystals

to 100 parts, by weight, of water. The solution shall be neutralized by the addition of an excess of chemically pure cupric oxide (CuO). The presence of an excess of cupric oxide will be shown by the sediment of this reagent at the bottom of the containing vessel.

The neutralized solution shall be filtered before using by passing through filter paper. The filtered solution shall have a specific gravity of 1.186 at 65°F . (reading the scale at the level of the solution) at the beginning of each test. In case the filtered solution is high in specific gravity, clean water shall be added to reduce the specific gravity to 1.186 at 65°F . In case the filtered solution is low in specific gravity, filtered solution of a higher specific gravity shall be added to make the specific gravity 1.186 at 65°F .

As soon as the stronger solution is taken from the vessel containing the unfiltered neutralized stock solution, additional crystals and water must be added to the stock solution. An excess of cupric oxide shall always be kept in the unfiltered stock solution.

(d) *Quantity of Solution.* — Wire samples shall be tested in a glass jar of at least two (2) inches inside diameter. The jar without the wire samples shall be filled with standard solution to a depth of at least four (4) inches. Hardware samples shall be tested in a glass or earthenware jar containing at least one-half ($\frac{1}{2}$) pint of standard solution for each hardware sample.

Solution shall not be used for more than one series of four immersions.

(e) *Samples.* — Not more than seven wires shall be simultaneously immersed, and not more than one sample of galvanized material other than wire shall be immersed, in the specified quantity of solution.

The samples shall not be grouped or twisted together, but shall be well separated so as to permit the action of the solution to be uniform upon all immersed portions of the samples.

(f) *Test.* — Clean and dry samples shall be immersed in the required quantity of standard solution in accordance with the following cycle of immersions.

The temperature of the solution shall be maintained between 62 and 68°F . at times during the following test:

First : Immerse for one minute, wash and wipe dry.

Second : Immerse for one minute, wash and wipe dry.

Third : Immerse for one minute, wash and wipe dry.

Fourth : Immerse for one minute, wash and wipe dry.

After each immersion the samples shall be immediately washed in clean water having a temperature between 62 and 68° F. and wiped dry with cotton waste.

In the case of No. 14 galvanized iron or steel wire, the time of the fourth immersion shall be reduced to one-half minute.

(g) *Rejection.* — If after the test described in section “F” there should be a bright metallic copper deposit upon the samples, the lot represented by the samples shall be rejected.

Copper deposits on zinc or within one inch of the cut end shall not be considered causes for rejection.

In case of a failure of only one wire in a group of seven wires immersed together, or if there is a reasonable doubt as to the copper deposit, two check tests shall be made on these seven wires and the lot reported in accordance with the majority of the sets of tests.

NOTE. — The equipment necessary for the test herein outlined is as follows:

Commercial copper sulphate crystals.

Chemically pure cupric oxide (CuO).

Running water.

Warm water or ice as per needs.

Carbona, benzine, or turpentine.

Glass jars at least 2 inches inside diameter by at least 4½ inches high.

Glass or earthenware jars for hardware samples.

Vessel for washing samples.

Tray for holding jars of stock solution.

Jars, bottles, and porcelain basket for stock solution.

Cotton waste.

Hydrometer cylinder 3 inches in diameter by 15 inches high.

Thermometer with large Fahrenheit scale correct at 62 and 68°.

Hydrometer correct at 1.186 at 65° F.

Filter paper.

Objections to the Standard Copper Sulphate Test. — In the authors' opinion there are grave objections to the copper sulphate test as carried out under either of the above specifications. The attack on the zinc coating which is made by the copper

sulphate is most active when the wire is first immersed in the solution and slows down to almost zero toward the end of the immersion. This slowing effect is of course due to the growing accumulation of deposited copper on the surface of the zinc. After the wire is withdrawn and wiped at the end of one minute the action starts off rapidly again on the section immersion only to again slow down as before. The consequence of this action is that it is quite usual to find a sample that will stand a three-minute immersion without failure, whereas an additional one second plunge after wiping will suffice to completely plate the surface with adherent copper. It follows from this that the test as carried out is not giving the copper sulphate an opportunity to exert its maximum effect throughout the period of the test. In order to obviate this difficulty one of the authors carries out the test under the following specifications which have been found to yield fairly concordant results:¹

The clean wire sample is immersed with a quick motion in the copper solution, and at the end of exactly five seconds quickly withdrawn and at once dipped into pure water and wiped. The immersion should be timed with a stop-watch if possible. As long as no copper is visible plated out on the iron, the five-second immersions are repeated until the copper deposit which begins to form wipes off with difficulty. At this point a series of rapid two-second immersions are made, with alternate wipings, until a bright metallic copper surface, which cannot be wiped off the wire, appears. The total time of immersion in minutes and fractions of a minute is taken as an indication of the percentage of zinc carried by the wire. Thus, if 150 seconds' immersion were necessary to reach the end point, the weight of the galvanizing would be called 2.5 per cent. It must be remembered that although the results of this test are approximate only, their value depends entirely upon careful accuracy in following out the directions.

It will readily be seen that the authors' method of making the test will give much lower results than those obtained under the commercial specifications given above. On the other hand, the results will be more accurate and more comparable. One great objection, however, to the more accurate method is that so much more time is consumed in carrying it out. In a wire mill in which samples are being tested from every bundle of wire made, this is a serious consideration.

¹ Cushman in appendix to Farmers' Bull., 239, U. S. Dept. Agr.

Walker has very recently published some interesting and valuable data on the testing of galvanized coatings. He criticises the copper sulphate test in the following words:

Walker's¹ Contribution to the Testing of Galvanized Coatings.—“When the copper sulphate reaction is used in testing galvanized iron it is assumed that the speed of solution of the zinc is a direct function of the time of immersion, and by the number of one-minute immersions necessary to dissolve the zinc from the iron and to deposit a film of bright copper thereon, the thickness of the zinc can be estimated. It will be seen that this method measures the thickness of the coating only at its thinnest point, and that the assumption is made that no bright copper will be formed until the iron base is reached. To appreciate the limitations of this test, it is but necessary to note the structure of the three classes of zinc-coated iron.”

“A polished oblique section of ordinary hot-galvanized iron etched with iodine reveals three distinct layers. First, a coating of zinc, which varies in thickness in accordance with the temperature of the zinc and the amount of squeezing or wiping applied to the article before the zinc solidifies; second, a distinct layer of a zinc-iron alloy, termed alloy B, which varies in thickness with the temperature of the zinc bath and length of time the iron was subjected to it; third, the iron base itself. Between the zinc and alloy B there is generally a second alloy, alloy A, which is a thin, discontinuous layer, richer in zinc than alloy B, and between the iron and alloy B is a third alloy, relatively unimportant, which is very rich in iron, alloy C.

“The structure of wet-galvanized iron is comparatively simple, the layer being practically pure zinc.”

“Sherardized iron, on the other hand, presents a relatively complex structure. The metallic zinc penetrates the iron, forming deep layers of the alloys B and C, and in place of alloy A there occurs a number of compounds, as yet unidentified. Upon the surface there is generally a layer of relatively pure zinc, although frequently the process is carried to the point where only a deep layer of alloys is formed. When examined under the microscope this alloy is seen to be covered with deep cracks or fissures as though the alloy in forming had contracted. It is thus apparent that in testing galvanized iron made by these different processes we are dealing with three very different materials.”

¹ Electro-chem. and Met. Ind., VII, 10. 440.

Walker's Desiderata for a New Test for Determining Durability or Resistance to Corrosion. — "It is the present purpose to treat of zinc-coated iron with regard only to its durability or resistance to corrosion, and not to its tensile strength. From this standpoint a test should, if possible, indicate the following:

- (1) The uniformity and thickness of the zinc coating;
- (2) the continuity of the coating with reference to pin holes;
- (3) the purity of the zinc, and
- (4) the toughness and ductility of the coating.

The corrosion of pure zinc in water is very slow. If, however, the zinc is in electrical contact with any material upon which the hydrogen can be liberated, the corrosion of the zinc is relatively rapid. The iron-zinc alloy B, and the iron itself, are both surfaces on which this depolarization action can take place, and, hence, so long as neither the iron nor the alloy is exposed, other things being equal, the zinc coating will not corrode. The importance, therefore, of maintaining a uniform coating of metallic zinc upon the iron can be appreciated.

To determine whether the ratio of the time of immersion required to produce a bright copper surface was in reality a measure of the thickness of the zinc coating, samples of galvanized sheets were obtained and tested. The weight of zinc per square inch area was determined by dissolving the zinc from the sheets without attacking the iron-zinc alloy. This can readily be accomplished by heating the galvanized sample, together with a piece of metallic iron, in boiling caustic soda until the generation of the hydrogen ceases. As might be expected, the ratio between the time of immersion required to show the presence of bright adherent copper and the amount of zinc present per unit area depends upon the uniformity with which the coating of zinc is spread upon the iron base. In the case of 14 pieces of galvanized sheet iron, for example, the average ratio found was 23, while the greatest variation in either direction was but 20. This test, therefore, so far as indicating the uniformity of the coating and measuring the thickness of the zinc are concerned, is fairly satisfactory; but alloy B is always indicated as iron, and hence, when the test is applied to sherardized articles, very erroneous and misleading results may be obtained.

The presence of the channels or pin holes caused by the free iron surface coming in contact with the zinc and causing it to pass

into solution cannot be detected by the copper-sulphate method, as these pin holes down through the zinc to the iron fill up with black, spongy copper and cover up the bright copper spot at the bottom.

The purity of the zinc cannot be determined, as the bright copper particles precipitated by this method are so small that they are lost in the mass of black, spongy copper.

Finally, the fourth factor, the toughness or the ductility of the coating, cannot be determined, due to the same tendency of the spongy copper to cover up the bright copper deposits, which indicate cracks extending down through the zinc coating to the alloy or iron underneath."

Walker's Test for Detecting Pin Holes and Cracks.—"The relation between the presence of pin holes in the zinc surface and cracks due to a brittle coating and the durability of the structure as a whole has not heretofore been studied, largely because no method of detecting these imperfections has been available. The following phenomenon serves as a basis for such a test. If a piece of zinc be placed in a strong solution of caustic soda heated to about 100° C. no action is noticeable. If now the zinc be touched with a piece of iron, hydrogen is liberated in great volume from the iron. Small cracks in the zinc coating may be easily detected in the same way."

"Ordinary hot-galvanized ware is generally very free from imperfections of this kind, while wet-galvanized ware, on the other hand, is frequently very porous, generating hydrogen at numberless small points over its entire surface. Theoretically, the best electroplated surface should be that carrying the greatest weight of zinc per unit area, deposited at the slowest rate. That is, the lower the current density at the cathode in plating, the less porous will be the deposited metal, and the thicker this dense deposit is the better protection will it be. A great many tests on electroplated zinc-coated iron were made, the samples varying in both these particulars. In every case, those deposited most rapidly were the most porous, and the results showed that the time of plating was more important than the weight of zinc per unit area, although there was a minimum below which it was not safe to go."

Walker and Campbell's Test for Determining the Combined Effect of Imperfections.—"As the rapidity of hydrogen generation

from zinc is a function of the presence of an alloy of zinc and iron, hence the more impure the zinc coating, the more rapid will be its solution in acid. Accordingly, the impurity of the zinc, the presence of pin holes and cracks, and the thinness of coating, are all factors which act in an accumulative way to increase the rate at which hydrogen is generated when the zinc surface is exposed to acid. This method has been developed by Mr. Charles L. Campbell in his thesis for the B. S. degree at the Massachusetts Institute of Technology, and found to give very concordant results. The apparatus employed may take any convenient form, it being but necessary to expose a known area of the zinc coating to a standard acid solution under uniform conditions and to measure the hydrogen generated per minute. In almost every case a sharp maximum is reached, giving the resultant of all the different factors which make for rapid dissolution of the zinc. Thus, in a series of wet-galvanized sheets, those electroplated for 15 minutes reached a maximum of 7 cu. cm. in 3 minutes; those plated for 30 minutes a maximum of 14 cu. cm. in 10 minutes, while those plated for 45 minutes showed a rather poor maximum of 6 cu. cm. in 30 minutes. In many samples of sherardized product there were two maxima on the curve showing the amount of hydrogen generated per minute. This indicates that there is first an action between the outside zinc coating and the iron-zinc alloy, and later a well-defined action between the alloy and the iron."

"Service tests with galvanized iron are of necessity very slow at best, and the relation of the above phenomenon to the real durability of the material can be determined only after a number of years. Something can, however, be learned by the study of ware which has already been exposed for sufficient time to determine its durability. Most of the material available for the purpose was in the form of fence wire; from a study of these the following conclusions are drawn":

First, Thickness of Coating.—"In every instance where a very durable fence was found, the coating of zinc proved to be relatively very thick. On the other hand, the wire fences which showed marked corrosion in from one to two years proved to have almost no zinc on the iron, the zinc color being due to a layer of alloy alone. It is doubtless true that the purity of the iron used in the wire itself plays an important part in determining the ultimate durability of a fence, yet in the opinion of the writer the

thickness of the zinc coating calls for more immediate attention. The modern method of close mechanical wiping the wire as it emerges from the zinc bath produces too often a wire covered not with zinc but only a thin layer of electro-negative iron-zinc alloy, which affords but little protection to the iron. To produce a wire with a liberal coating of zinc would, of course, cost more, both on account of the extra zinc and on account of a somewhat smaller production per machine."

Second, Purity of Zinc. — "It is probably a necessary consequence of hot galvanizing that the zinc becomes somewhat contaminated with dissolved iron. It is apparent that this should be kept at a minimum in order that the coating should be of maximum durability."

Third, Flexibility of the Zinc Coating. — "The important objection to placing a thick coating of zinc upon wire used for fencing is that such a coating cracks off when running through the machine. This objection applies only to those wires which are subjected to very sharp bends or turns. It is possible that by passing the zinc-coated wire through dies or under grooved rolls that the crystalline condition of the zinc could be destroyed and the flexibility and ductility materially increased."

Walker sums up his results as follows:

1. "The copper sulphate immersion test is of value in determining the uniformity of coating and relatively the thickness of coating in hot and in wet-galvanizing products; but it is worthless in the case of sherardized products, and gives no idea of other important factors involved in the durability of the structure.

2. By immersing a galvanized product in hot, strong caustic soda, the presence of any unprotected iron may easily be detected, however small such area may be.

3. The weight of zinc per unit area apart from the zinc-iron alloy may be analytically determined by dissolving the zinc from the plate through treatment with hot caustic soda while in contact with metallic iron.

4. Theoretically, the rate at which hydrogen is evolved when the galvanized product is immersed in dilute acid should indicate its relative durability; inferior products should reach a maximum in a few minutes compared with a much longer time for better products.

5. In the very important matter of fencing wire, while the

purity of the iron used is of consequence, a more immediate necessity is a heavier coating of zinc on the wire.

6. The flexibility of a zinc-coated wire may possibly be increased by mechanically working the wire in rolls or dies, to destroy crystallization in the zinc coating."

The authors desire to record here that the conclusions reached by Walker are in complete accord with their own opinions, as will appear in the following paragraphs which were written before Professor Walker's publication was available.

Circumstances Affecting the Weight of the Zinc Coating and the Corrosion of Fence Wire. — Galvanized sheet metal from different sources show generally less variation than wire in the weight of zinc carried. The reason for this is perfectly obvious: the sheets leave the spelter bath through light rollers and are set aside to cool. The rate of cooling affects the size of the "spangled" crystalline structure of the zinc coating, but generally no effort is made to thin or smooth the zinc surface. Wire, on the other hand, is either smoothed or actually wiped as it leaves the spelter bath. This fact has an important bearing on the durability of wire galvanized by the hot-dip process. Telegraph, telephone, and in fact all straight-line wires which are not designed to be fabricated into any form of woven wire, are usually smoothed by drawing through a loose bed of damp charcoal or sand. Such wires can easily, and should always, be made to stand four-minute immersion in the copper sulphate test, this is sometimes held to mean that the wire carries about 4 per cent. of zinc. This represents about the practical limit of the quantity of zinc that iron in any form can be made to carry in a smooth coating. If the coating is unsmoothed the zinc will to some extent collect in lumps and nodules which add to the cost without increasing the efficiency of the coating. The American market demands a form of wire fencing which for various reasons is not used to any extent in Europe. This is the woven wire or fabricated fence, so many types of which are in common use in this country. In the usual practice, wire for these fences is galvanized before the weaving or welding process of fabrication is begun, and if the coating of zinc is thick, it is liable to crack in the bends formed by the weaving machines. If a welding process is used too thick a coating of zinc interferes with the formation of strong bonds at the joints. For this reason it is customary to wipe the galvanized wire for

fabricated fences as it issues from the spelter bath with asbestos wipers. The result of this treatment is that this type of wire generally will not stand more than two-minute immersions in the copper sulphate test, and the authors have tested many samples that would not stand even this length of time. Undoubtedly this is one of the principal contributory causes of the rapid corrosion of woven-wire fences.

It is well known to every one familiar with the process of galvanizing wire that it is not possible to get as heavy a coating of zinc on light-gage wires of small diameter as on heavier wires. It would therefore be unreasonable, even if unwiped wire could be used in fabricated fencing, to expect a number 14 gage wire to stand the copper sulphate test as long as a number 9 or 7 gage wire. The only cure for the fence problem will consist in the public demand for fences fabricated of heavy gage wire carrying the maximum weight of zinc consistent with the practical possibility of its manufacture. In the authors' opinion no wire of lighter gage than number 9 should ever be used in a fence if durability is an important consideration. From an economical point of view, it is cheaper to cut down the number of wires in a fence rather than to lighten their gage and weight. The authors would further suggest that the slight crackling of the zinc coating at the bends of wire or other flexible material should no longer be considered as objectionable, as it has been in the past. In the effort to reduce this tendency to crack the galvanizers have been tempted to wipe closer and closer, until in some of the modern practice almost no zinc is left at all. Cracking at sharp bends as a matter of fact is a good test of honest galvanizing and shows that at least a fairly heavy coating of zinc has been applied. Zinc is electro-positive to iron and when the two metals are in contact and wet with a corroding solution, zinc will be destroyed and iron will be protected. The extension of the sphere of influence of the protecting zinc will depend upon the severity of the attack. The more corrosive the action, the larger the protected area, but the more rapid the destruction of the zinc. This can easily be shown by soldering a button of zinc to a steel plate and immersing the whole in water or various corroding solutions. The appearance of such an experiment is shown in Fig. 32. From this point of view a heavily zinc-coated wire, even with slight cracks at the bends, should be preferred to a very light-coated wire which

exhibits a smooth appearance to the eye. The test wire fences which are about to be described show that after fourteen months' exposure to the Pittsburg atmosphere the cut-off ends of the galvanized wires are all bright and free from any appearance of rust, although, of course, no zinc covers the cross-section of the cut-off ends. Since this is the case, slight cracking of the superficial coating of galvanized material should not be made the "bugaboo" of the honest galvanizer. It will often be noted that the cut ends of galvanized iron will rust in a warehouse if under cover, and will remain bright for long periods when exposed to more corrosive influences in the open. This apparently contradictory observation is accounted for by what has been said above. If the attack is very slight, such as is produced by condensed moisture from the atmosphere, the protective electrolytic action of the zinc does not come into play, leaving the iron to slowly coat itself with a superficial layer of hydroxide. Under the more severe outdoor conditions, however, the zinc continues to protect the iron in its neighborhood as long as it lasts.

Summary of possible improvements in the hot-dip process:

(1) Careful annealing of the wire and avoidance of stresses and strains.

(2) Use of purer spelter and more careful attention to the drossing and scumming of the spelter bath.

(3) Control of the acidity of the fluxing or soldering bath, with the possibility of substitution of an alkaline or inert fluid.

(4) Development of methods for obtaining heavier coatings of zinc, with the possibility of devising a practical method for galvanizing wire fences after they are fabricated.

The Electrolytic or Cold Method of Galvanizing. — Since it is possible by means of the electric current to deposit a coating of zinc on iron which is practically free from other metallic impurities, it would seem that this method has some advantages over the hot-dip method. The fact that it has found and is maintaining a place in large industrial processes is the best indication that for certain purposes the method is successful. Like the hot-dip process, however, the cold electrolytic process has its weak points and is open to criticism. Burgess,¹ after an extended investigation, formed a favorable opinion of electro-galvanized material, but speaks of some of the disadvantages of the process

¹ Electro-chem. and Met. Ind., III, 1, 22.

as follows: "It is seen that to obtain the best quality of coating the disadvantages of the electrical method are brought out, the principal one of which is the great length of time required to apply the deposit. This can be remedied only by the use of high current densities, and with solutions at present available it seems impracticable to run the density beyond 18 or 20 amperes per square foot on account of the liberation of hydrogen and undesirable physical quality of the deposit produced. In the tests made, 14.4 amperes per square foot was taken as best representing practical conditions where a cold, unagitated solution is used. With this current density the metal may be deposited with a current efficiency of nearly 100 per cent.

"A serious limitation upon the electrolytic process as at present applied is that after the coating has reached a certain thickness there is a tendency for it to become rough and crystalline, and this tendency makes it extremely difficult to apply a coating having more zinc than 30 grams per square foot."

In another place the same investigator says: "A great difficulty lies in securing an even distribution of current over the object being plated, as demonstrated on corrugated sheet iron and other irregularly shaped articles. This causes, also, greater thickness and roughness around the edges.

"The tests of durability show that the best results are attained with solutions operated as nearly neutral as possible, and that the addition of free acid, which seems desirable for keeping a clear solution, not only decreases the current efficiency, but also materially reduces the efficiency of the zinc as a protection.

"There seems, therefore, abundant opportunity for improvement in zinc-plating solutions, even though present methods are giving good results industrially. Such improvements may come through the discovery of new compositions for the bath which will enable higher current densities to be used, thicker deposits to be obtained, and greater stability and uniformity of operation acquired. Circulation has been suggested as an improvement, and it is to be expected that the advantages which efficient agitation gives in copper depositions may also be realized with zinc-plating vats.

"The adherence of zinc coatings to iron is frequently ascribed to an alloying which is supposed to take place. The tests for adherence indicate that no such alloying occurs, either with hot or

electrolytic galvanizing, since the tenacity with which the coatings adhere is far less than would be expected if alloying existed."

Although it is true that the electro-galvanizing process provides a method of obtaining a closely adherent coating of zinc which is not likely to be alloyed with other metals, evidence collected by the authors tends to show that material protected by this method is no more resistant to corrosion than that coated by hot dipping. Mowry¹ has claimed as the result of experiment that electrolytic coatings are inferior to those made by the hot-dip method. The difficulty seems to be, as has already been pointed out, that certain impurities from the electrolytic bath are included in the deposited zinc and become accelerators of corrosion. The Trunkhahn² system of electro-galvanizing attempts to surmount this difficulty by avoiding an acid bath, and by keeping the electrolyte saturated with nascent hydrogen by a special method which it is claimed prevents oxidation of the coating, renders it more dense, and prevents the occlusion of corrosion-stimulating impurities from the electrolyte. The authors have not been able up to the present time to determine to what extent the claims made for this system of electro-galvanizing are justified as far as the durability of the coatings are concerned.

The Vapor Deposition Process. — The Cowper-Coles³ method of vapor galvanizing which is known as Sherardizing is a development of recent years. There is a considerable literature on the subject as shown in Appendix B which should be consulted for full information.⁴ "Vapor galvanizing is distinctive from all other forms of galvanizing inasmuch as the vapor of zinc is employed for coating metal surfaces instead of dipping them into molten zinc or into an aqueous solution through which a current of electricity is passed. Two forms of vapor galvanizing are practised, namely the 'zinc dust process' and the 'molten zinc vapor process.' In the first process the zinc dust and the iron articles to be coated are placed in an air-tight iron drum, which is heated in a gas-fired furnace to obtain a temperature within the drum of about 600° F. The length of time at which the drum is kept at that temperature depends on the thickness of the coat

¹ Mowry, *Iron Age*, 77, 352.

² See *Dingler's Polytech. Jour.*, 320, 47, 1 (1905).

³ *J. Soc. Chem. Ind.*, 28, 399-403.

⁴ *Chem. Abs.*, 3, 23, 2792.

required. The drums are emptied over an iron grid, which retains the zinc-coated article and allows the zinc dust to collect into a receptacle in order to use it over again for charging the drums. The coating is distributed evenly and is alloyed with the iron surface. According to claims made, the alloy is non-corrosive and does not rust even when the zinc surface has been removed by abrasion. The advantages of vapor galvanizing are said to be that it is cheaper than the ordinary hot galvanizing, forms a better protection, and at the same time enables screw threads and machine work to be coated with an even distribution of zinc, so that the parts fit together properly. In the 'molten zinc process' the materials to be coated are placed in a cage or hollow drum which is slowly rotated inside an outer cylinder, composed of wrought iron, to ensure an even coating. The metallic zinc is heated by means of gas, or any other suitable means, to a temperature sufficiently high to volatilize the zinc at the same time that hydrogen or any other gaseous reducing agent is forced into the apparatus. A modification of the vapor process is applied to the inlaying and decorating of metallic surfaces which surpasses all other methods in artistic effects. Furthermore it has the advantage that a number of metals may be blended together, which hitherto has been impossible, and alloys of many tints and colors can be obtained in one operation."

Sherardized material has not been available in this country for a sufficient time for complete tests of durability to be made. The vapor deposition process avoids some of the above-mentioned difficulties of the other two methods, but it is by no means certain that it does not introduce other undesirable factors. Although zinc is electro-positive to iron, certain alloys of zinc and iron are said to be electro-negative and have in addition to this a higher solution pressure than pure zinc. If these alloys are formed in this process the main purpose of using zinc as a protective agent is defeated. On the other hand, the dry process can be used for galvanizing articles that have fine interstices, such as the threads of pipe fittings, etc., so that while it may not prove to be efficient for wire and some other special forms of iron, it will probably have a distinct field of usefulness.¹ The results of durability tests of

¹ Since the above paragraph was written Sang has described his Electro-Cementizing process for wire. This is a modified form of the vapor deposition method. See Proc. Elec. Chem. Soc., XVI, 257.

sherardized material will be watched with interest. One curious fact that has been noted in connection with exposure tests on sherardized material is the peculiar black sooty color that is assumed by the exposed surfaces. After once acquiring the black surface, sherardized articles appear to be very resistant to corrosion.

*Tests of Galvanized Wire.*¹ — At the request of one of the writers a number of interesting tests have recently been undertaken for the purpose of ascertaining the relative resistance to corrosion of steel wires of varying chemical composition, and also to show the relative value of protective coatings.

With these ends in view twelve samples of galvanized steel wire were manufactured by the American Steel and Wire Company. They have been put up in the form of fence and exposed to the action of the weather on the grounds of Carnegie Technical School at Pittsburg (Fig. 33). These twelve samples fall into three groups, which will be described in the order in which they were made.

The first sample was a wire of the following composition:

	Per Cent.
Carbon	0.66
Manganese84
Sulphur028
Phosphorus016

This was made by the basic open-hearth method. The ingots were cast July 23, 1908, and were reheated and rolled into billets the same day. On the following day they were again heated to redness and rolled into $\frac{1}{8}$ -inch rods. One billet was taken at random from the lot for the purpose of this test. The rod after cooling was cleaned by immersion in hot dilute sulphuric acid, then rinsed with water and dipped into milk of lime. After drying, the rod was drawn cold into 9-gage wire. It was then galvanized by passing it through a furnace in which it was heated to dull redness, and then into a bath of hydrochloric acid containing zinc chloride, and lastly into a bath of molten zinc. This wire was not wiped; that is to say, it was allowed to retain as much zinc as

¹ The expenses of these tests were incurred by the American Steel and Wire Co., and the fences were mounted on the grounds of the Carnegie Technical School at Shenley Park, Pittsburg. The tests have been placed under the general supervision of Committee U of the American Society for Testing Materials. A description of them is included here as the intention is to keep them in place for a number of years until final failure occurs.

would adhere to it. This sample was designated C-1, and it is purposed to test it against any of the low-carbon, low-manganese wires to be described later, and which may for this purpose be regarded as C-2.

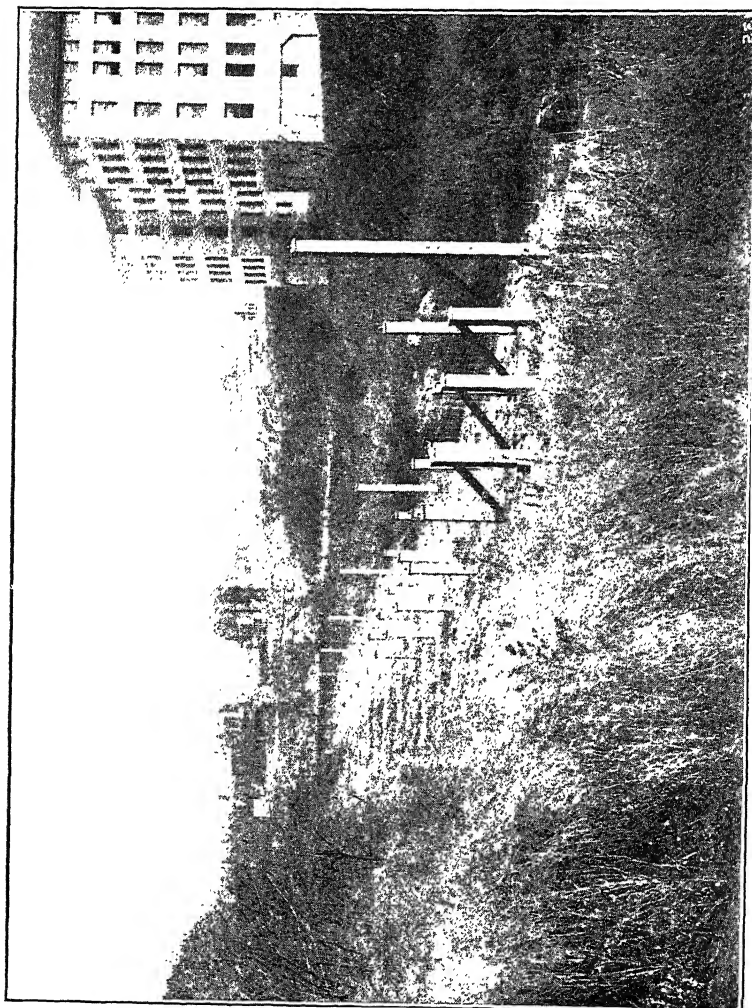


FIG. 33. — Showing the Pittsburg wire fence tests as first erected, Sept. 23, 1907.

The second group consists of six samples of "American" style, 8-strand fabricated fencing, 45 inches high. The object of this group is to determine the effect, if any, of segregation of the

impurities in the iron. Therefore the six samples were taken from the same heat. The steel was made at the same mill and on the same day as sample C-1, but by the Bessemer process, and was cast in six ingots. As these ingots were rolled, two billets were taken from the top of the first ingot, two billets from the middle of the first ingot, and two from the bottom of the first ingot. These three pairs of billets were marked, respectively, A-1, A-2, and A-3. Similarly, from the last ingot of the heat two billets were taken from the top, two from the middle, and two from the bottom. These three pairs of billets were marked, respectively, B-1, B-2, and B-3. These were all rolled hot into rods, and after cooling and cleaning, in the manner described above, were drawn into wire. The six samples were each divided into three portions. About half of each sample was drawn into 11-gage wire, a quarter of each sample into 9-gage wire, and the remaining quarter into 12-gage wire. This was because these three sizes of wire are all used in making the standard "American" fence, the 9-gage for the top and bottom horizontal strands, the 11-gage for the intermediate strands, and the 12-gage for the vertical connecting wires. Immediately after being drawn the wire was galvanized in the same manner as described for sample C-1, except that on emerging from the molten zinc it was wiped by a mechanical device which left a thin, smooth coating of zinc on the steel. A separate piece of fencing about 300 feet in length was then woven from each of the samples. These six pieces of fencing then represented the top, middle, and bottom of the first and last ingots of the heat, respectively. The samples were not analyzed separately, but an analysis of the heat as a whole showed percentages as follows:

	Per Cent
Carbon	0.09
Manganese55
Sulphur045
Phosphorus092

The third group consists of five samples of basic open-hearth steel showing increasing amounts of manganese from 0.07 per cent. to 0.37 per cent. These were all made in one furnace, between August 18 and August 22, 1908. The process of manufacture throughout was identical with that employed on the sample designated C-1, except that the wire was wiped during

the process of galvanizing. These five samples were all drawn to 11-gage and are designated by their "heat numbers," which are given here together with the analyses.

ANALYSIS OF FIVE SAMPLES FORMING THE THIRD GROUP.

Heat Numbers	Carbon	Manganese	Sulphur	Phosphorus
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
S118	0.05	0.12	0.014	0.014
S11904	.07	.014	.014
S12005	.16	.010	.010
S12105	.24	.018	.018
S12206	.37	.013	.016

All the wire described above was shipped to Pittsburg, Pennsylvania, and between September 23 and September 26, 1908, was put up in the grounds of the Carnegie Technical Schools. The site assigned for this purpose is a level strip of ground at the bottom of a deep and narrow natural depression to the north of the quadrangle of school buildings. Because of this location none of the wire will be exposed to the action of wind, but all will show the effects of fog and dampness, which are very prevalent in this hollow.

The fence was put up in an extremely substantial manner. The posts are 2 by 8 inches, dressed oak; the corner posts are 8 by 8 inches, sunk 3 feet in the ground. The lower ends were painted with a mixture of benzine and asphalt, and the portion above ground with ordinary lead paint. The post holes were filled in with concrete.

There are four parallel lines of posts, as shown in Fig. 33, 3 feet apart and 275 feet long. These lines run almost due east and west. The one farthest north is called row No. 1, the next row No. 2, the next row No. 3, and the line farthest south No. 4. The arrangement of the wire on these posts is as follows:

- On the north side of row No. 1 is placed sample A-1.
- On the south side of row No. 1 is placed sample A-2.
- On the north side of row No. 2 is placed sample A-3.
- On the south side of row No. 2 is placed sample B-1.
- On the north side of row No. 3 is placed sample B-2.
- On the south side of row No. 3 is placed sample B-3.

On the north side of row No. 4 at the top are 8 strands of 8119.

On the north side of row No. 4 at the middle are 8 strands of C-1.

On the north side of row No. 4 at the bottom are 8 strands of 8118.

On the south side of row No. 4 at the top are 8 strands of 8122.

On the south side of row No. 4 at the middle are 8 strands of 8121.

On the south side of row No. 4 at the bottom are 8 strands of 8120.

In the first three rows the posts are 15 feet apart, in the fourth row 30 feet apart. The wire was all stretched as tightly as possible to prevent sagging, and none of it is less than 1 foot above the ground.

In addition to the test fences described above, a number of panels have been mounted on either side of the original rows in order to test different methods of providing protective coatings for ordinary steel wire fences. One panel of American style woven-wire fence is galvanized by the cold or electroplating process; another panel is made of double galvanized wire carrying about the same weight of zinc as is usually specified for telegraph wire. This galvanizing has been done by a special adaptation and variation of the ordinary hot-dip process, and has not been subjected to the acid bath before galvanizing. A third panel is coated with zinc by the Sherardizing process. A number of panels, in part galvanized by the ordinary hot-dip process, and in part ungalvanized, have been protected by painting with various protective paint coatings. The formulæ of these stimulative and inhibitive paints will be published in a special report. All of these extra panels have been mounted in exactly the same manner and side by side with the samples already described in the foregoing, and the tests should in the course of time yield results of great value. A key to the arrangement of all the panels is shown in Fig. 34.

Preservation with Tin.—Roofing, cans, and tinned utensils of all kinds depend for their preservation on a metal coating which, though not electro-positive to iron, has such a low solution tension that it is known to be practically incorrodible. The principal difficulty encountered in the use of this metal is that it seems impossible to apply it economically to the surface of steel

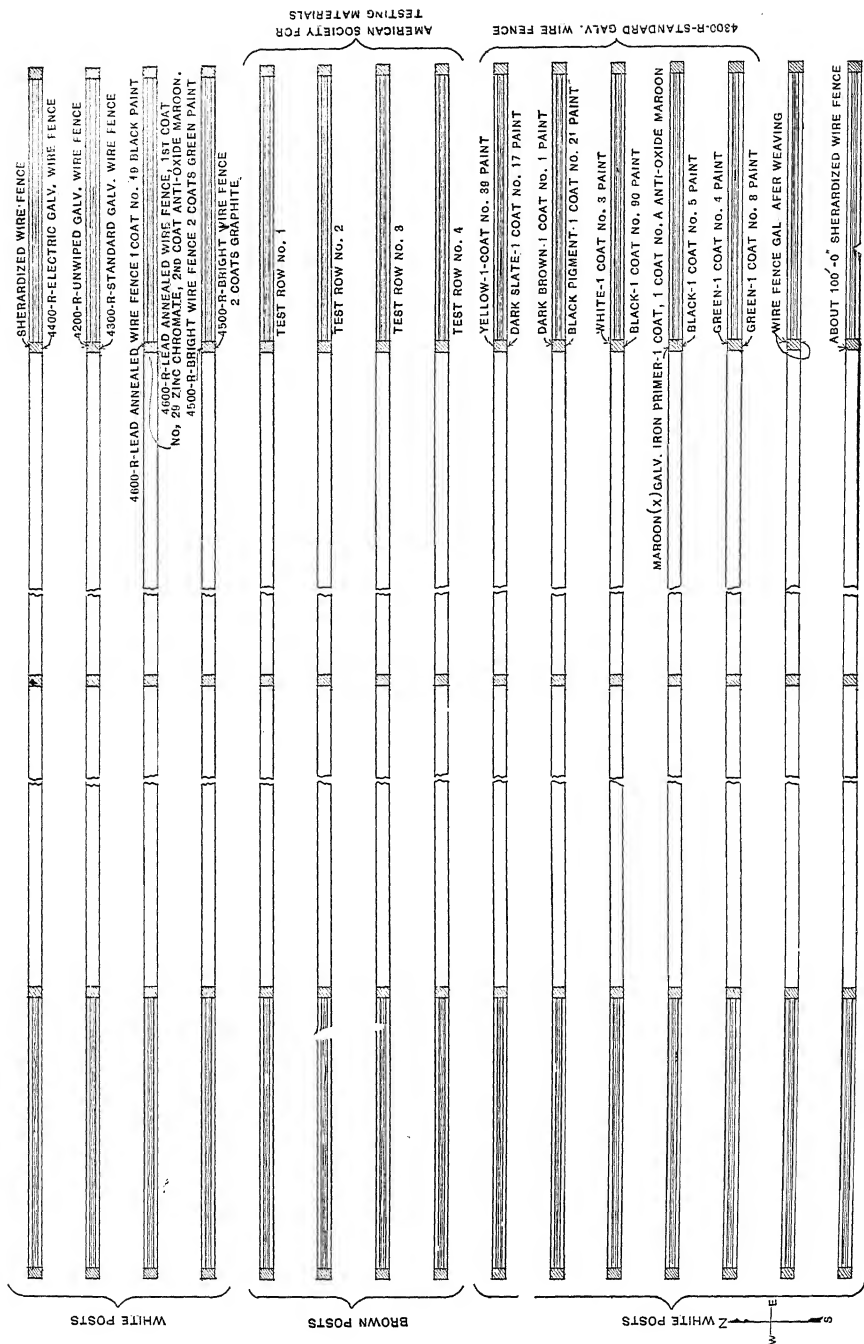


Fig. 34. — Diagram of steel wire fences at Pittsburg.

so that pinholes shall not exist in the coating. Walker has shown this by an ingenious modification of the ferroxyl test.¹ A slightly acid solution of gelatin containing a small amount of potassium ferricyanide is flooded, while hot, upon the surface of the tin plate to be tested. The gelatin becomes hard upon cooling, and in a very short time every pinhole on the tin surface is marked by a spot of Turnbull's blue. The results obtained by Walker are illustrated in Figs. 35 and 36. They are made even more

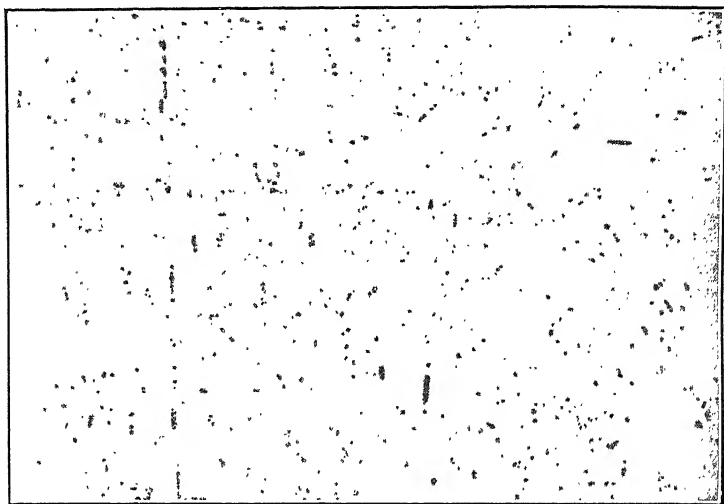


FIG. 35. — Showing Walker's method of determining pin holes in tin plate.

interesting by comparison with the actual corrosion of a tin plate under service conditions shown in Fig. 37. After the number and position of the pinholes is known, it becomes possible to study ways and means of eradicating them. Hot rolling and ageing of the plates under pressure are among the solutions that have been suggested in the hope that the pinholes will disappear.

The passage of the Food and Drugs Act of 1906 has had a curious and interesting bearing on the tin-plate industry in its application to canned goods. Artificial coloring matter is debarred by this law, and it was found that the natural color of preserved food-stuff is reduced and destroyed by the action of the tin. In

¹ Jour. Iron and Steel Inst., 1, 79 (1909).

the effort to meet this difficulty the can manufacturers sought to use less tin, and also to lacquer the tin plate so as to prevent its contact with the fruit and vegetable juices. The formation of pinholes has gone on rapidly, however, so that it is not an unusual occurrence to find tinned preserves discharging their juices in tiny streams through small holes resulting from rapid corrosion. Walker's more recent researches on this subject have already been described in a previous chapter.

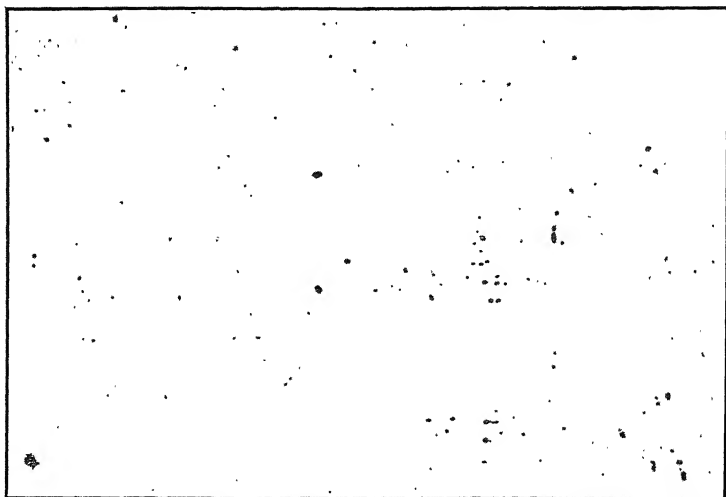


FIG. 36. — Showing Walker's method of determining pinholes in tin plate.

Preservation with Copper, Lead, and other Metals and Alloys. — It is possible to make copper-coated steel, but this makes an efficient and rust-resistant material only when the coating is thorough and homogeneous. Methods are being developed to extend the use of copper for this purpose, and it is now applied to wire as well as to sheet and plate metal. If the cost is not a prohibitive factor, there would seem to be no reason why steel protected in this way should not come into more general use. It follows, however, from the electrolytic theory of corrosion that if openings in the copper coating occur so that water can penetrate to the point of contact, the corrosion of the iron will go on very rapidly. Tassin,¹ speaking for the new metallurgical product

¹ Jour. Industrial Chem., 1, 9, 670.

known as copper-clad steel, makes the following claims: "Copper and steel in the presence of moisture form a galvanic couple, and the corrosion of the steel proceeds with great rapidity. The resistance to corrosion of copper-clad so far as the copper coating is concerned is, of course, the same as that of copper. But, in

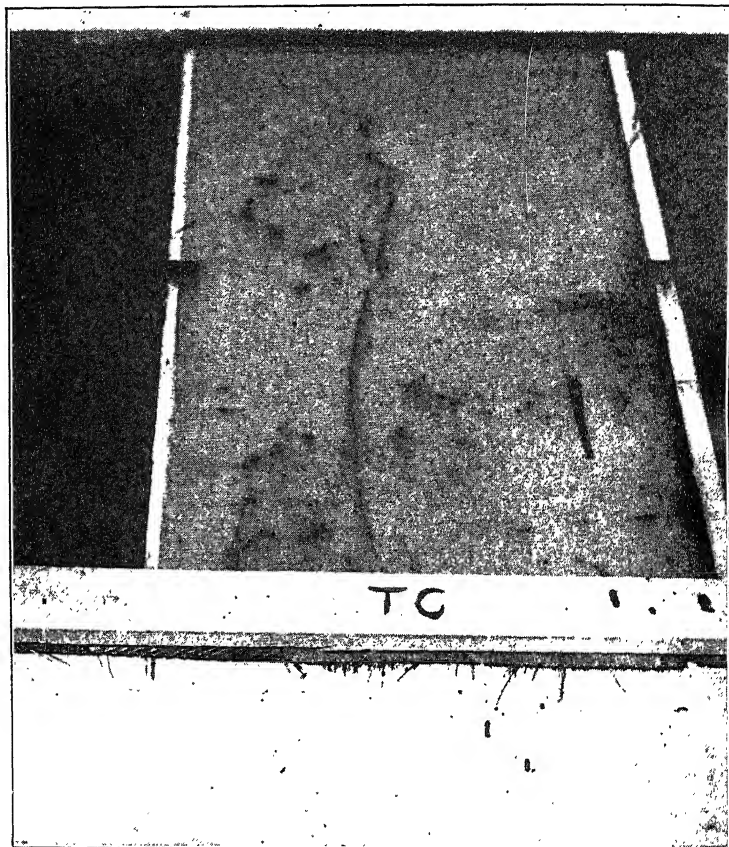


FIG. 37. — Charcoal iron tinned plate, showing the corrosion lines.

view of the marked galvanic action set up between copper and steel, it would be assumed that corrosion would quickly occur at the exposed ends, and be a constant factor so long as an electrolyte was present. This supposition is not so, at least in the presence of fresh or salt water. Test samples placed in water, through which a current of air has been allowed to bubble

continuously for three months, demonstrated that after a certain period of time, somewhere between 15 and 40 days, corrosion practically ceases, as shown by taking the loss in weight of the tests at varying periods. It is believed that this stopping of corrosion is a result of the following conditions:

“After a certain amount of rust has been formed, it appears that a thin film of copper mixed with some copper oxide is plated out or deposited between the iron oxide and the unattacked steel, and that this film will act as a preservative coat as long as it remains intact. If broken, further oxidation sets up and the process simply repeats itself. While it is true that the corrosion on the end of a wire is not a factor in its life, yet the corrosion of the end of a relatively large diameter may become very serious. If the above observations hold true on larger sizes (so far it has not been tried on sizes above $\frac{3}{8}$ in.) it will have quite a bearing on material suitable for marine work. Tests along this line are now being carried out, and the evidence to date points to a confirmation of the observations made on the smaller sizes.”

Lead has to some extent been used for covering iron, and for certain purposes this material is useful. It is doubtful, however, whether the application of lead for this purpose will find a very wide field of usefulness. Terne plate covered with an alloy of lead and tin is, of course, extensively used. There have been many complaints recorded in regard to the rapid corrosion of this material, to which much that has been said in previous paragraphs of this book about other forms of protection will apply.

Many other alloys have been proposed and experimented with for the protection of iron. In more recent work the effort is made to change the electro-negative character of lead or tin by producing electro-positive alloys of these metals that will have the proper physical characteristics to warrant their use as protective coatings. Among these may be mentioned an alloy of lead and antimony, and of tin with antimony and aluminum. None of these special alloys have as yet come into very general use.

Processing after Manufacture. — A number of metallurgical processes, which depend upon the production of a fully oxidized surface on iron and steel, have been in use for a number of years and are too well-known to require description. Among these are

the Bower-Barf and Wells methods of producing a surface of magnetic oxide. If perfectly coherent and homogeneous such a surface is, of course, unrustible. The protection of the metal depending as it does upon a coating that is strongly electro-negative to iron, it follows that any manipulation or accident that injures the continuity of the covering surface must necessarily lead to accelerated and deep corrosion. This fact together with certain other practical difficulties has confined the use of these processes to special cases where protection from corrosion is a matter of prime importance. It is claimed for the process that it is specially valuable for builders' hardware, domestic articles, wrought-iron grilling, railings, and the better class of scroll and fancy work. It has also been used for pipe of various kinds, and can be used on general structural material of a rigid nature. It could not, of course, be used with wire or flexible forms, owing to the brittle nature of the magnetic oxide.

The well-known Russia iron, which is in common use for stove-pipes, locomotive casings, etc., depends upon a similar oxide coating. When taken care of, iron treated in this way will last for many years without failure from corrosion.

Sang¹ in an article on the inoxidation processes for protecting iron and steel gives the following information: In the Barf process the articles to be coated are heated to 1000° and steam superheated to 538° is injected into the coating chamber. In the Bower process, producer gas rich in carbon monoxide is said to reduce the red oxide obtained by air treatment or by subjecting the work to acid fumes. In the Bower-Barf process the articles to be coated are heated in a closed retort to 871°, after which superheated steam is injected which forms a coating of the black magnetic oxide. The operations are repeated alternately until a sufficient depth of oxidation is obtained. The cost of treatment is expensive and ranges from \$5 to \$20 per ton. It is claimed that enamel will hold tenaciously to iron so treated and that paint can be applied without trouble. The coatings are said to resist acid fumes better than galvanized iron; they are not affected by solutions of copper sulphate. This method has been used to some extent for coating pipes in order to make them withstand corrosion. A modification of the Bower-Barf is the Wells process, which consists of introducing the steam and carbon monoxide at

¹ Electro-chemical Metallurgical Industry, 7, 351-3.

the same time. In Gesner's process, a compound of hydrogen, iron, and carbon is said to be deposited on the iron. Steam at low pressure is introduced through a red-hot pipe into the coating retort, which is kept at a temperature of 538° to 649° , while some hydrocarbon gas is allowed to enter slowly. By this means the higher oxide of iron is reduced and the surface carbonated. The charge for so treating small articles is said to range from 4 to 7 cents per pound, and for large pieces about 1 cent per pound. The Dewees Wood's process is similar to Gesner's process. Ruffington employs potassium nitrate in his method for oxidizing the surface of the iron. Claudius uses a solution of a manganese compound for the production of durable black coatings or patina. Hydraesfer's process is essentially similar to Gesner's, but requires only one furnace operation.

A number of electric processes have been proposed, both for oxidizing the surface of steel and also for producing a passive condition of the surface. One of the authors called attention to the possibility of the use of electric currents in producing a passive condition some years ago. Meritens' method uses a bath of distilled water at a temperature of 70° to 80° and applies a weak current. The nascent oxygen which is given off in the presence of the hydrogen occluded in the metal produces a film of black oxide of iron. It is, however, impossible to produce a deep coating unless a sufficient amount of hydrogen is present in the iron, and on this account it is generally necessary to run the article first as cathode in order to enable it to absorb hydrogen. Lately Toch has been investigating the use of electric currents to produce a more or less lasting passive condition of the surface. This work has not yet been published in detail, but it is understood to consist in making the iron to be treated an electrode in an alkaline solution using a current of large amperage at low potential. Krassa¹ works in a hot caustic soda solution and makes the iron the anode. Strong currents make the anode passive at once, while weak ones cover it with a black coating of Fe_3O_4 . To get active iron again the specimens must be boiled for a long time. Further work along these lines will be watched with interest.

Several other methods have been proposed from time to time for processing after manufacture in order to make the surface

¹ Zeit. Electro Chem., 15, 490.

resistant to corrosion. The Coslet process is said to consist in immersing the iron in a hot, phosphorized solution containing an iron compound. The surface, it is claimed, is converted into a ferroso-ferrie phosphate, which is to some extent resistant to corrosion. Jouve¹ has called attention to the fact that iron containing 10 per cent. of silicon is not attacked by acids, and, therefore, such material should theoretically be unrustible. The authors have confirmed this deduction by experiment, and found that iron containing 10 per cent. of silicon is almost incorrodible. Unfortunately, such a metal is not workable, and has peculiar properties. Since silicon is much like carbon, chemically speaking, it would seem as if it might be worked into the surface of steel by modifications of some of the processes used for case-hardening with carbon.

Unprotected Steel. — A large proportion of the iron and steel which is in use cannot, from the very nature of the service to which it is put, be protected from corrosion. To this class belong rails, heavy chains, implements, boiler tubes, etc. The only hope of meeting this particular phase of the problem consists in the improvement of metallurgical processes, to the end that perfectly homogeneous metal, as free as possible from segregation, may be manufactured. It is well known that some of the alloyed steels, such as nickel steel, are very highly resistant to corrosion. The same thing is probably true of the chromium, vanadium, and chromium-vanadium steels. Unfortunately, such materials are too costly to be used on a large scale, although there is always the possibility that some alloy or combination will be discovered which will be at the same time comparatively inexpensive and incorrodible.

The Corrosion of Boilers. — One of the most important phases of the technical preservation problem is the necessity for preventing the pitting of boilers and boiler tubes. In a bulletin published some years ago, one of the authors² stated that the pitting of boiler tubes was probably due to electrolysis, and it was shown that Wood had reached the same conclusion in 1894. Wood³ said: "That there is a continual electrical action of a most complex character present in all boilers under steam can scarcely

¹ Engineer, 1908, Vol. CVI, p. 397.

² The Corrosion of Iron. Bul. 30, Office of Public Roads, U. S. Dept. Agr. (1897).

³ Am. Soc. Mech. Eng. Trans. (1894), 15, 998.

be doubted, and the same action, but less apparent, is possibly present in all constructions of iron when the different members formed of iron and steel of various compositions, made by different processes after various torturing methods of manufacture to bring them to the desired shape, are assembled and put into duty under strains and conditions foreign to their nature. It would be strange indeed did not some electrical energy manifest itself and call for some palliative if not protective means of arresting decay."

Recently Burgess¹ without reference to previous authorities has reached the same conclusion. Burgess describes an investigation which shows the importance of electrolytic action in boiler corrosion, and states that if electrolytic action were entirely absent or could be entirely neutralized, there would be practically no internal corrosion. Iron may itself set up electrolytic couples even if it is not segregated owing to physical strains occasioned by previous heat treatment. Burgess suggests as a possible remedy the use of an external iron bar maintained as an anode by a current from a dynamo, the negative pole of which is connected to the boiler. This suggestion had been made many times before² in connection with boiler tubes and also for the protection of pipe lines; it has not, however, as far as the authors are aware, been very generally adopted.

The expedient of using metallic zinc in boilers to overcome local electrolytic effects in the iron by producing a still greater electrolytic effect at the almost exclusive expense of the more positive zinc is well known and has been in use for a long time. Great difficulty has, however, been experienced in maintaining good metallic contacts between sufficiently large surfaces of the two metals under the conditions which maintain in a boiler; moreover, as has been previously shown, the protective action of zinc takes place only in a restricted area.

The most practical method for protecting boiler tubes depends upon the exclusion of oxygen from the feed water. It has been shown that oxygen plays an important contributing role in the electrolytic corrosion of iron. In order to remove this action, the use of pyrogallol, amidol, tannic acid, and other reducing agents has been proposed, but far more practical ways than this are known. Feed-water heaters in which all the dissolved gases

¹ Jour. Western Soc. Eng., 14, 375.

² See Cushman in Journal Iron and Steel Inst., 1 (1909), 37.

may be removed are not difficult to design, and if these were made a necessary adjunct of all boilers there would be fewer cases of boiler-tube corrosion to cope with.

Special Cases Met with in the Preservation of Iron. — In the opinion of the authors the most interesting and significant discussion of recent date on a special corrosion problem is to be found in the Transactions of the American Institute of Mining Engineers for the years 1907 and 1908. The special significance of this discussion lies in the fact that it exhibits the more or less divergent opinions of a number of engineers and experts of wide experience. We find in it the views of engineers who are considering their problems in the light of the electrolytic explanation of corrosion, as well as the opinions of those who refuse to consider that any form of electrolysis is a factor.

Theories are manifestly of little value unless they can come to the aid of those who are charged with the great industrial problems of the world, and it is in the court of practical experience that a working theory must be tried and either proved or found wanting. At the same time it frequently happens that an engineer will at first consider as "new-fangled" or "fanciful" a new theory only because he has not fully grasped its meaning or recognized its application to his problem. The authors have thought it best to include the entire discussion in an appendix¹ as its re-reading will undoubtedly stimulate thought. Indeed, the problems discussed should be reviewed in the light of the modern theories and explanations of corrosion.

As has been pointed out, the technical preservation of iron and steel presents a great number of separate problems, each one of which requires special consideration and different treatment. As an instance of this, it may be stated that the cases of wire, of ships' bottoms and boiler tubes involve special difficulties, in which the environment and conditions of service are so different as almost to constitute three separate problems. Nevertheless, the same underlying principles apply to the general problem of the corrosion of iron in all its phases. It has been the object of the authors to make these principles clear in the foregoing pages. The protection of the great bulk of finished iron and steel must inevitably remain a paint problem, and to the consideration of this the remaining portion of this book will be devoted.

¹ Appendix A, p. 279.

CHAPTER VII

RELATION OF PIGMENTS TO THE CORROSION OF IRON

THE many theories which have attempted to explain the rusting of iron, during the last century, have stimulated a large amount of original research on the relation of various pigments to the corrosion problem. In the course of the investigations undertaken, the subject of protective coatings for iron and steel was naturally brought into prominence and received a considerable amount of attention. The study of protective coatings for iron has led many paint manufacturers, as well as scientific investigators, to make a closer study of the causes of corrosion. It is evident that the electro-chemical explanation of corrosion must have a direct bearing on paint problems.

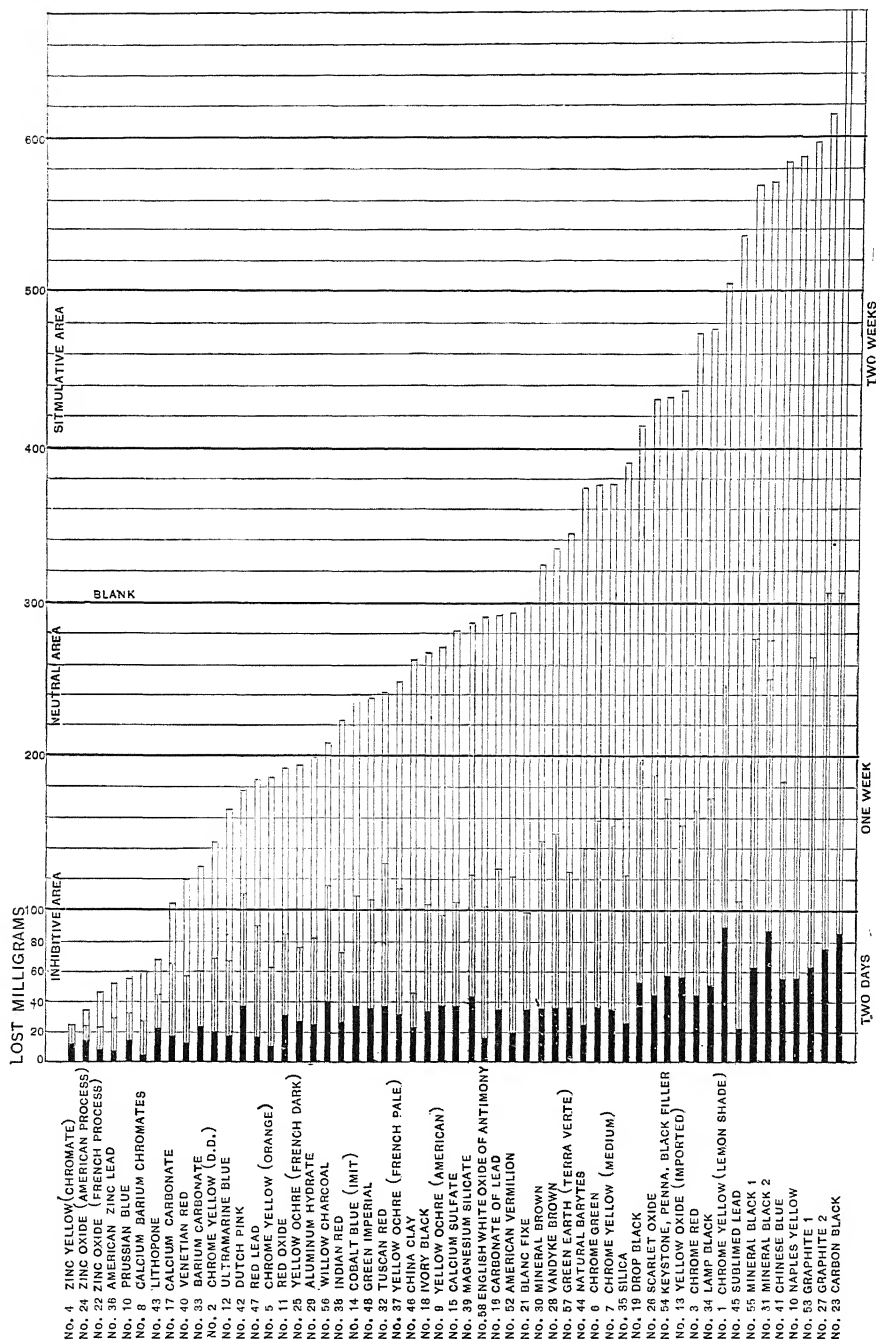
In the course of researches carried on by one of the authors upon the corrosion of iron, it was found that certain substances in contact with iron possessed the property of exciting electrical action and stimulating corrosion, while still other substances exhibited a tendency to inhibit or prevent corrosion. Bichromates of soda and potash were found to be the most eminent examples of the so-called "inhibitives," and it was found that as long as steel or iron remained in contact with these salts, even in fairly dilute solution, rusting could not take place. This naturally suggested the preparation and use of slightly soluble chromates as pigments. It was found that the chromic acid salts could be precipitated with certain other compounds to produce chromates applicable as pigments. A series of these compounds were prepared and tested; but it soon became apparent that while some afforded protection to steel, others did not. The raw materials used, the method of preparation, the amount and character of the contained impurities, together with other factors, had a marked influence upon the efficiency of these compounds. It was even found that a series of chrome salts, all of which theoretically should have possessed inhibitive value, were in many cases actually stimulative.

Testing Pigments in Water Suspension. — The results obtained

from these investigations led to a series of experiments, first suggested by Thompson, in which the effort was made to determine the relative inhibitive value of a number of typical pigments for application to iron. A series of fifty of the most important pigments used in the manufacture of paints was therefore procured and submitted to test. The apparatus in which these pigments were tested consisted of a series of eight-ounce bottles, into each of which was placed a measured amount of pigment, afterward adding the same amount of distilled water to each bottle. Into each bottle was then placed a strip of steel, numbered and carefully weighed. The bottles were then connected up in series by the use of rubber stoppers and bent glass tubing, through which a constant current of washed air was passed for a period of three weeks. At the end of this time the train of bottles was disconnected, the steel plates removed, washed off, carefully brushed with a tooth brush, to remove any extraneous or adherent pigment particles, and afterward dried and carefully reweighed. A loss in weight represented the amount of iron which was removed by corrosion. From the results obtained it was possible to tentatively divide the pigments into three groups.¹ The pigments which caused the most active corrosion were termed "rust stimulators," those which showed the least action were termed "rust inhibitors," while those which were found to be intermediate in the group were called "inerts."² The results were charted, Fig. 38, showing the position of each pigment tested, and the results proved so interesting that it was decided by Committees "E" and "U" of the American Society for Testing Materials to carry on a supplementary series of experiments. A considerable quantity of pigments similar to those used in the first test were collected in the open market, and samples of each, from the original package, were put in cans, carefully marked, stamped, and forwarded to members of the Committee, who had volunteered to repeat the work. A series of small plates of steel of the same size, cut from the same sheet of metal, and all stamped with numbers running from 1 to 50, were also supplied to each investigator. A description of the apparatus used for the test was also sent to the members of the Committee.

¹ See Cushman, *The Inhibitive Power of Certain Pigments on the Corrosion of Iron and Steel*. Proc. Am. Soc. Testing Materials, VIII, 605 (1908).

² Some objection was made to this use of the word "inert" and the joint Sub-committee of Committees U and E, Am. Soc. Testing Materials, adopted the word "indeterminate."



The results obtained by the various investigators, working independently and in different laboratories, were afterwards compared at a special sub-committee meeting, called for the purpose. The agreement between the results obtained by the several investigators corroborated the results of the original work, and appeared to indicate that the theory of inhibitors should have some practical application.

Effect of Impurities and Other Factors Governing Nature of Pigments.— Since this work was done, so much progress has been made following this line of investigation that it now seems possible for certain rules to be formulated in regard to the inhibitive value of various pigments. Not only the nature of the pigment itself, but also the quantity and kind of impurities contained in it, decide in which one of the three groups a given material must be classed. The solubility of the pigment, and the ease with which it is ionized when brought into contact with water, are also important considerations. If the pigment is of a basic nature, and therefore tends to increase the number of hydroxyl ions in solution, it is sure to be in the inhibitive list, provided the concentration of the hydroxyl ions is sufficiently high to furnish protection. If the pigment is acid in nature, or contains any free acid which is easily hydrolized, it is quite certain to appear in the stimulative group.

The question naturally arises as to whether a pigment which has been shown to possess active stimulative properties may be mixed with a pigment possessing inhibitive values, and in this manner become inert or non-stimulative. This depends largely upon the percentage of inhibitive pigment added. In some cases the addition of a large quantity of inhibitive pigment would be of little value, as the following statement already published by one of the authors illustrates:¹ "If the surface of iron is subjected to the action of two contending influences, one tending to stimulate corrosion, and the other to inhibit it, the result will be a breaking down of the defensive action of the inhibitor at the weakest points, thus localizing the action and leading to pitting effects."

It is interesting to note that the two samples of Prussian blue which were included in the tests described in a previous paragraph showed widely divergent results, one proving to be an inhibitor and the other a stimulator of corrosion. As a matter of fact, these two samples of Prussian blue were prepared by different

¹ Proc. Am. Soc. Testing Materials, 1908, VIII, 606.

methods. In one, acid impurities were sure to have been included. As has been already pointed out in a previous chapter, it is impossible to throw down a colloidal precipitate from a solution without the inclusion of ions and salts from the mother liquors. The methods of manufacture used in these two Prussian blues served as an advance indication that one would appear in the stimulative, and the other in the inhibitive class, and they were so marked. The fact that the result of experiment brought out this relation presents additional evidence in support of the general theory.

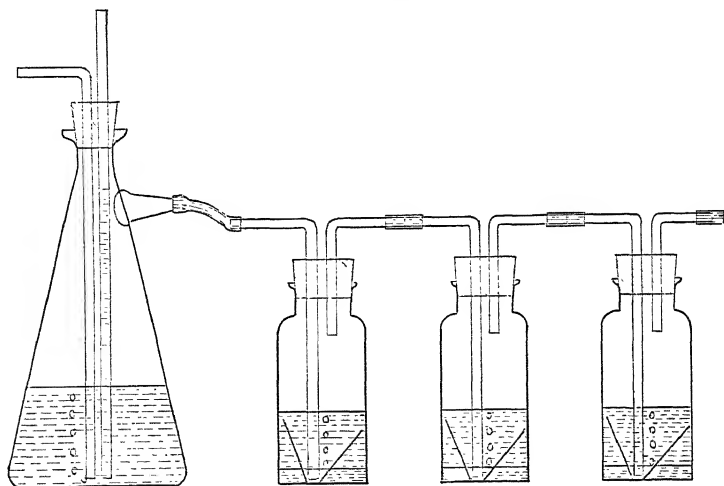


FIG. 39.—Apparatus used in testing inhibition value of pigments.
(Cushman.)

It is well known that a good working theory should enable an investigator to predict to some extent in advance what the results of experiment should show. Thus with the theory of periodicity of atomic weights in hand, Mendeléeff was enabled to predict the existence of unknown elements which were subsequently discovered. Although it is not claimed that the observations in regard to the Prussian blues are of the same order of magnitude as the predictions of Mendeléeff, nevertheless the results obtained are none the less suggestive.¹

The results of these tests are given below. The apparatus used in their determination is illustrated in Fig. 39.

¹It is of course not yet shown that the relative durability of paint coatings under service conditions will agree with these results, but the authors think that the point made is none the less interesting.

CHART OF FINDINGS OF MEMBERS OF COMMITTEES "E" AND "U", AMERICAN SOCIETY FOR TESTING MATERIALS. LOSS OF STEEL IN GRAMS IN TESTS CARRIED OUT ON PIGMENTS TO ASCERTAIN THEIR VALUE AS RUST INHIBITORS.

Pigment	Gardner	Cush-	Walker	Cush-	Walker	Aver'ge
	No. 1 20 days	man Nos. 1 & 2 10 days	P. H. No. 2 7½ days	man No. 2 10 days	W. H. No. 1	
1 Zinc Chromate.....	.0050	.0300	.0094	.0130	.0396	.0194
2 Zinc and Barium Chromate0153	.0468	.0034	.0140	.0351	.0229
3 Zinc and Lead Chromate0094	.0277	.0153	.0085	.0620	.0246
4 Zinc Oxide.....	.1524	.0296	.1002	.0085	.0504	.0682
5 Zinc Lead White0842	.171	.0515	.0856	.0456	.0876
6 Barium Chromate.....	.233	.0101	.0429	.0094	.1932	.0978
7 Ultramarine Blue0247	.3185	.0137	.1865	.0496	.1186
8 Chrome Green (blue tone)0860	.2269	.0548	.1240	.2346	.1453
9 Prussian Blue (Inhibitive)1438	.2267	.0448	.1130	.2671	.1591
10 Lithopone0160	.3791	.1274	.17921754
11 Willow Charcoal1694	.2795	.1439	.136	.2110	.1880
12 Litharge4325	.1932	.0309	.15842038
13 Dutch Process White Lead...	.2040	.2895	.1781	.1150	.2743	.2122
14 Quick Process White Lead...	.2120	.3352	.1288	.1848	.2274	.2176
15 Calcium Sulphate3966	.2143	.1759	.1597	.2174	.2328
16 Prince's Metallic Brown.....	.3774	.2620	.1983	.1408	.1974	.2352
17 Orange Mineral French3950	.2724	.1495	.1467	.2526	.2432
18 Calcium Carbonate (Whiting).	.3828	.3620	.1384	.2380	.1208	.2484
19 Sublimed Blue Lead.....	.3177	.3425	.1001	.2365		.2492
20 Lemon Chrome Yellow2767	.4067	.1365	.1972		.2543
21 Orange Chrome Yellow2826	.4203	.1700	.1907	.2150	.2557
22 Medium Chrome Yellow.....	.4090	.3767	.1319	.1763	.2288	.2645
23 Chrome Green3265	.3670	.1348	.1453	.3521	.2651
24 Venetian Red2682	.4756	.1955	.2375	.1564	.2666
25 Bone Black3392	.3245	.0921	.1413	.4401	.2674
26 Asbestine2394	.4025	.1748	.2240	.3405	.2762
27 Keystone Filler3560	.4651	.1366	.3349	.1481	.2881
28 Orange Mineral (American) ..	.4416	.4336	.1719	.2065	.2315	.2970
29 Umber.....	.1365	.5961	.1498	.3817	.2403	.3009
30 China Clay3493	.4770	.1248	.2445	.3212	.3034
31 Calcium Carbonate Precipitated	.3574	.4910	.1828	.2625	.2616	.3111
32 Red Lead3112	.3555	.1495	.1717	.5707	.3117
33 Prussian Blue (Neutral).....	.3584	.4463	.1218	.2415	.4173	.3171
34 Indian Red3546	.3739	.2617	.1905	.4334	.3228
35 American Vermilion4328	.4147	.2612	.1877	.3387	.3270
36 Sublimed White Lead4176	.5856	.0982	.2372	.3116	.3300
37 Sienna.....	.2876	.5432	.2949	.3085	.4462	.3761
38 Naples Yellow.....	.6482	.4800	.1512	.2347	.3846	.3797

CHART OF FINDINGS, ETC. — *Continued*

Pigment	Gardner No. 1 20 days	Cushman Nos. 1&2 10 days	Walker P. H. No. 2 7½ days	Cushman No. 2 10 days	Walker W. H. No. 1	Average
39 Prussian Blue (Stimulative)	.5113	.4559	.2055	.2195	.5202	.3825
40 Mineral Black3050	.8018	.2017	.3529	.3353	.3993
41 Barytes4454	.5883	.2547	.3841	.5636	.4472
42 Natural Graphite4342	.5437	.2606	.3173	.7165	.4545
43 Bright Red Oxide3878	.7896	.2920	.3707	.4429	.4566
44 Acheson Graphite5262	.6337	.3723	.2789	.5095	.4641
45 Ochre4022	.8408	.2119	.43154716
46 Carbonith White2655				.7152	.4904
47 Carbon Black5003	.6955	.4069	.3751	.5716	.5099
48 Precipitated Blanc Fixe5247	.8806	.3132	.5085	.5064	.5467
49 Lamp Black7180	.3038	.2838	.7096	.6257	.7294

CLASSIFICATION OF PIGMENTS BASED ON RESULTS OF TESTS.

Inhibitors	Indeterminates ¹	Stimulators
Zinc Lead Chromate	White Lead (quick process,	Lampblack
Zinc Oxide	Basic Carbonate)	Precipitated Barium
Zinc Chromate	Sublimed White Lead (Basic	Sulphate (Blanc
Zinc and Barium	Sulphate)	Fixe)
Chromate	Sublimed Blue Lead	Ochre
Zinc Lead White	Lithopone	Bright Red Oxide
Prussian Blue (In-	Orange Mineral (American)	Carbon Black
hibitive)	Red Lead	Graphite No. 2
Chrome Green (Blue	Litharge	Barium Sulphate
tone)	Venetian Red	(Barytes)
White Lead (Dutch	Prince's Metallic Brown	Graphite No. 1
process)	Calcium Carbonate (Whiting)	Prussian Blue (Stim-
Ultramarine Blue	Calcium Carbonate (Precipi-	ulative)
Willow Charcoal	tated)	
	Calcium Sulphate	
	China Clay	
	Asbestine	
	American Vermilion	
	Medium Chrome Yellow	

¹ See note, page 164.

Electrical Conductivity of Paint Films. — Certain objections to the foregoing tests have been made on the ground that they were made in water solutions in which the pigments were sus-

pended. It was claimed that pigments which might stimulate or cause corrosion in the presence of water would have no such action when enveloped in an oil medium. It was said that the oil acted as an envelope for the pigment particles, and being in itself a non-conductor of electricity should prevent electrolytic action taking place upon iron. While this criticism is worthy of the most careful consideration, it appeared to the authors that the objectors had not paid attention to the well-known fact that linseed oil films have the power of absorbing both water and carbonic acid. For this reason the oil film cannot be considered a non-conductor of electricity, and must depend to a large extent upon the pigmentary substances with which it is reinforced. In order to get further data on this interesting subject, the following experiments were carried on by one of the authors.

A series of glass slides such as are used in microscopic work were painted with a number of separate pigments ground in linseed oil. After the paint films were thoroughly dry, small strips of copper were attached to the opposite ends of the paint films, and these were in turn attached to the wires of an ordinary dry cell, a galvanometer being included in the circuit in order to measure the current passing through. It was found that absolutely no current could pass a perfectly dry paint film, and the galvanometer needle remained in its original position, at zero. The glass slides were then removed from the apparatus and immersed in water for four hours, during which time the films were inevitably penetrated to some extent by water. The action of rain and weather exposure upon painted metal surfaces in the open of course produces a similar result. The slides were then removed from the water and, after being carefully wiped, again inserted in the apparatus and tests made to determine whether any passage of current took place. It was found that those pigments which are naturally good conductors of electricity permitted to a slight extent the passage of current, which was shown by the deflection of the galvanometer needle. Those pigments, on the other hand, which are not good conductors of electricity, permitted so little current to pass that the needle remained practically stationary. The pigments referred to as being conductors of electricity, which were used, belong in the carbonaceous group, and appeared in the stimulative class, as may be seen by reference

to the foregoing table. These experiments seem to indicate that when iron is painted with the so-called stimulators of corrosion, if for any reason water finds its way into the oil film, electrolysis, with the resulting current flow, is able to take place, and is sure to cause active corrosion of the steel surfaces to which such pigments are applied. On the other hand, it appears to the authors that it is not unreasonable to conclude that the use of insulating pigments which prevent the flow of current, even when the film of lynoxyn, in which they are enveloped, is to some extent damaged, will tend to check the corrosion of painted metal surfaces.

If the immunity from rust, of painted surfaces, depends mainly upon the inhibitive properties of the pigments with which the steel is coated, it is fair to believe that this immunity from attack will be reinforced by providing that the principal base content of the pigment shall be a good non-conductor of electricity. In addition to the nature of the pigment, the character of the vehicle must also be considered. Inhibitives in liquid form may be incorporated with the vehicle, and thus a double protective effect produced. The use of a paint inhibitive in both pigment and vehicle antagonizes the forces that cause corrosion, and the greater the inhibitive value of the pigment and the vehicle, the greater will be the defensive action working against the factors which produce corrosion and rapid decay.

Water-shedding and Excluding Properties of Pigments. — A careful study of the nature of paint films has shown that some pigments produce and lend peculiar properties to the oil in which they are enveloped, which give to the resulting films an excluding or a water-shedding nature. An excluding paint is one that has the property of excluding and preventing the admittance of water to the underlying metal, thus protecting the steel from the water, which is the essential medium in which corrosion can alone take place. A water-shedding paint is one which, because of its peculiar physical character, appears to show a certain inability to become wetted. Plates painted with pigments of the latter class dry very soon after rains, while paints made of another type of pigments retain upon the surface drops of rain which tend to be absorbed by the paint coating and ultimately work through to the metal. The porosity which is generally noted in every dried paint film may be prevented by the use of gums, so that a coating is formed which is a good excluder, but

such coatings are not always the best water shedders. The size of particle of the various pigments used, and their adaptability for filling the pores of the film, is an extremely important consideration in the composition of a paint which will form films, both excluding and water-shedding. Linseed oil when used by itself, will be found to possess neither excluding nor moisture-shedding properties. The film will soon become tacky, and show a peculiar blistered appearance, which indicates the spots where moisture has penetrated, and results in the formation of a soft, easily disintegrated film.

It would appear from the conductivity experiments which have been described in a previous paragraph that the carbonaceous pigments, which sometimes are good excluders, often fail to serve their purpose in the end, for the unctuous nature which has given them their water-shedding value sooner or later disappears, and the ultimate break-down of the coating admits moisture.

That other authorities have accepted this explanation of the authors is shown in part by the following citation from Toch:¹ "It is universally admitted that the presence of water is necessary before corrosion can take place, since this is the medium which contains or supplies the hydrogen ions which are necessary for interchange with the iron. Thus, in order to prevent rusting, you must either exclude water entirely, or have some substance present which will prevent the formation of the hydrogen ions. The only way in which this problem can be solved is by the application of a paint which will either protect the surface by being absolutely impervious to water, and therefore resistant to the hydrolizing action, or one which contains in itself either as a part of the vehicle or pigment some substance which can produce the passive state."

Moisture Penetration Tests of Paint Films. — The penetration of moisture into and through paint films is evidently to some extent dependent upon the peculiar nature of the pigments contained in the paint. Some paint films have the power of preventing the admission of water, while others containing different pigments seem to easily permit the entrance of moisture. A series of tests were designed by one of the authors, to determine the water-excluding power of a number of typical pigments,

¹ Trans. Amer. Electro-chem. Soc. XIV, 1908, 210.

when ground in oil and made into films. It has not been found possible up to the present time to devise a method of making films of absolutely even gauge. In the test which is about to be described there may have occurred a very slight difference in the thickness of the films.

A series of small glass bottles with wide mouths, holding about two ounces, were half filled with concentrated sulphuric acid, and paint films were tightly sealed over the mouths of the bottles, using Canada balsam. The bottles were then carefully labeled, numbered, accurately weighed on chemical balances, finally exposed to air saturated with moisture and kept at constant temperature under a large glass receptacle. The bottles were removed from the receptacle every week and weighed. The increase in weight, due to the amount of moisture which had penetrated the films, and which had been taken up by the sulphuric acid, owing to its hygroscopic nature, was thus determined.

In another series of bottles, lumps of calcium chloride were substituted for the sulphuric acid. The results obtained from these tests corresponded to those of the former series, and led to the conclusion that linseed oil films are undoubtedly porous, and also that certain pigments have the property of reducing this porosity to a greater extent than others.

As has been pointed out, however, this test cannot be used as an accurate measure of relative permeability, owing to the difficulty of making films of definite and constant thickness. The following table gives the results of the test:

MOISTURE EXPERIMENTS.

FIGURES GIVEN EXPRESS GAIN IN WEIGHT, *e.g.*, WATER ABSORBED

	7 days	14 days	21 days	28 days	35 days	49 days
Iron Oxides (with 2 per cent. Zinc Chromate and 2 per cent. Gum)	0.032	0.048	0.072	0.092	0.110	0.140
White Lead, D. D.	0.040	0.078	0.111	0.162	0.187	0.264
White Lead and Zinc Oxide	0.043	0.081	0.115	0.163	0.192	0.266
China Clay	0.044	0.086	0.122	0.182	0.219	0.317
Whiting	0.044	0.079	0.114	0.167	0.197	0.277
Zinc Oxide, Barytes and Blanc Fixe	0.048	0.092	0.125	0.183	0.190	0.290
Zinc Lead White	0.049	0.095	0.130	0.181	0.211	0.284
Red Lead	0.049	0.092	0.130	0.187	0.215	0.295
Basic Sulphate—White Lead	0.049	0.092	0.128	0.185	0.213	0.292

MOISTURE EXPERIMENTS. — (*Continued*)

	7 days	14 days	21 days	28 days	35 days	49 days
Zinc Oxide and Whiting	0.060	0.110	0.156	0.221	0.256	0.352
Zinc Chromate	0.064	0.121	0.176	0.270	0.298	0.417
Barytes and Zinc Oxide	0.064	0.118	0.169	0.240	0.278	0.386
Zinc Oxide	0.065	0.122	0.172	0.244	0.285	0.391
Calcium Sulphate	0.066	0.140	0.212	0.313	0.377	0.555
American Vermilion	0.069	0.140	0.202	0.311	0.349	0.501
White Lead, Barytes and Blanc Fixe	0.074	0.137	0.200	0.294	0.344	0.490
Barytes	0.074	0.138	0.202	0.298	0.336	0.466
Willow Charcoal	0.077	0.154	0.236	0.378	0.459	0.694
Lithopone	0.083	0.156	0.228	0.332	0.380	0.550
Carbon Black	0.084	0.168	0.250	0.391	0.448	0.654
Lead and Zinc Chromate	0.086	0.161	0.226	0.319	0.369	0.497
Chinese Blue (Stimulative)	0.092	0.185	0.276	0.405	0.470	0.671
Venetian Red	0.093	0.190	0.279	0.418	0.508	0.770
Natural Graphite	0.104	0.223	0.350	0.539	0.632	0.951
Medium Chrome Yellow	0.106	0.207	0.300	0.429	0.505	0.725
Bright Red Oxide	0.116	0.240	0.365	0.548	0.662	0.976
Barium and Zinc Chromate	0.116	0.211	0.298	0.430	0.481	0.660
Ultramarine	0.119	0.230	0.336	0.484	0.578	0.814
Prussian Blue (Inhibitive)	0.125	0.246	0.361	0.521	0.619	0.733
Raw Linseed Oil	0.143	0.300	0.449	0.679	0.803	1.201
Lampblack	0.199	0.411	0.641	1.033	1.234	1.873
Blanc Fixe	0.210	0.472	0.744	1.144	1.414	1.944

The pigments appear in this table in the diminishing order of their excluding values.

The action of a high-grade gum, in sealing up the pores and filling the interstices of a vehicle, is also indicated by this test. It will be found that iron oxide used alone appears about half-way down the list, while iron oxide, containing 2 per cent. of gum in addition to the linseed oil, was found to be an excellent excluder. The apparatus used is shown in Fig. 40.

Industrial Application of the Theory of Inhibitors. — That the manufacturer is rapidly coming to the realization of the value of the new theory of rust inhibition, as outlined in the preceding chapters, and is adapting it to commercial practice, is shown by the change that has been made in the formulas of several protective paints now on the market. Heckel¹ has said: "Out of

¹ Railway Age Gazette.

this mass of tentatively accepted facts has developed a provisional theory along which the more advanced manufacturers are now engaged in working out a new mode of procedure in the painting of steel.

"The theory is that rust-stimulating pigments should never be placed in contact with the steel surface, but that an inhibitive priming coat should always intervene. This inhibitive coating may be suitably compounded of the chromes, zinc oxide, white



FIG. 40.—Apparatus for Testing Permeability of Paint Films.
(Gardner.)

lead, red lead, willow charcoal, etc., among the inhibitors, or of any of the neutral or indeterminate pigments reinforced with a small proportion of the stronger inhibitors, such as zinc chrome, zinc oxide, zinc and lead chrome, etc.

"Over this priming coat the air — and moisture — excluding coats can then be safely applied; these coats being designed for protection only, with regard to inhibitive qualities."

Commenting on the action of gums in rendering paint films less porous, Perry states:¹ "Turning, therefore, to the conserva-

¹ Coatings for Conservation of Structural Materials. Bulletin No. 14, Scien. Soc., Paint Mfrs. Assn. of U.S.

tion of structural iron and steel, and to its rust inhibition through particular coatings, we have the problem of choosing the proper materials for manufacturing a paint which will both exclude the agencies of rusting, and which, when moisture and gases do penetrate the coating, will inhibit the iron from rusting; and we also have the problem of giving to the chemist, engineer, and architect some simple method of determining whether any given paint is, in at least rough measure, harmful, safe, or beneficial.

"In the case of structural steel we have a condition of the surface to be protected, essentially different from the conditions existing with lumber. Lumber, no matter how well kiln dried, invariably has some moisture in its structure. It has been absolutely demonstrated, and all technical men acquainted with the subject are agreed, that linseed oil, when dried to a coat of linoxyn, has voids or pores in it. The paint manufacturer uses a combination of pigments which largely fill these voids, but the most carefully prepared coat of paint for lumber, when the vehicle is linseed oil, without the addition of varnish, is always somewhat porous, and the moisture has some opportunity to pass out without blistering, etc.

"In the case of structural steel we have no moisture in the structural material to contend with,¹ as we have with lumber, and therefore we can safely add varnish gums in solution to the linseed oil, thus producing a more nearly water-proof coat to the agencies of decay. The action of the gum, diffused throughout the linseed oil by solution, is to help to fill up or fuse together the pores or voids, or, in other words, to render the linoxyn film more resistant to the entrance of moisture through the paint coating to the structural material. This is the conclusion reached from the standpoint of technical research, and practical experience has also demonstrated that those coatings which have been proved the best protection for steel have invariably contained a vehicle in which some gum or varnish material has been present."

In the above connection, Toch's² views on the subject of the

¹ With this statement the authors are not in complete agreement, as it has been contended that more or less moisture is always absorbed on the surface of iron and furnishes one of the many difficulties met with in the attempt to provide a perfect coating on iron. This point has been discussed in another chapter.

² M. Toch. *The Chemistry and Technology of Mixed Paints*, p. 87. D. Van Nostrand Co., New York, 1907.

physical characteristics of linseed oil films, and the part they play in corrosion, should be added: "There are questions in regard to the physical and chemical characteristics of linseed oil on which there has been considerable discussion and naturally a difference of opinion. The first is whether linseed oil dries in a porous film, and the second is whether linseed oil while drying goes through a breathing process and absorbs oxygen, and gives off carbonic acid and water." With reference to the porosity of the dry film of linseed oil, the same authority has stated:¹ "In a paper before the American Chemical Society on March 20, 1903, I gave it as my opinion that a dried film of linseed oil is not porous, excepting for the air bubbles which may be bedded in it, but that any dried film of linseed oil subjected to moisture forms with it a semi-solid solution, and the moisture is carried through the oil onto the surface of the metal. We then have two materials which, beyond a doubt, have sufficient inherent defects to produce oxidation under the proper conditions, and granted that the percentage of carbon dioxide in the air of the tunnel is not beyond the normal, the fact that carbon dioxide, together with moisture, would cause this progressive oxidation is sufficient warrant for the discontinuance of paints that are not moisture and gas proof. Lewkowitsch demonstrated in his Canton lectures that the fats and fatty oils hydrolized with water alone, and linseed oil is hydrolized to a remarkable degree in eight hours when subjected to steam. It can, therefore, be inferred that water would act on linseed oil without the presence of an alkali, and calcium hydroxide added to water simply hastens the hydrolysis, by acting as a catalyzer. This, then, bears out my previous assertion that a film of linseed oil (linoxyn) and water combine to form a semi-solid solution similar in every respect to soap, and inasmuch as we have lime, lead, iron, and similar bases present in many paints, it is almost beyond question that these materials aid in the saponification of oil and water."

In summing up the discussion of the possible porosity of paint films as presented above, the authors can only reiterate that the results of their experiments appear to them to furnish actual proof of the permeability of paint films by moisture. Whether or not the result is due to porosity must depend upon

¹ Journal of the Society of Chemical Industry (May 31, 1905), "New Paint Conditions Existing in the New York Subway."

just what is meant by that term. The formation of a solid or semi-solid solution must be dependent on the existence of molecular interstitial spaces. Whether spaces of these orders of magnitude should be called pores is quite beside the question as the final result is the same in either case.

Thompson's Work on Solubility of Paint Films.—That the solubility in water of various paint coatings must also be taken into consideration, as well as the inhibitive and excluding properties, seems to be indicated by the work of Thompson.¹ In a series of tests of oil films immersed in water, Thompson found that calcium sulphate was dissolved in great quantity from films containing this pigment. Thompson's method of conducting the solubility tests, as described by him, is as follows: "The paint is coated on antiseptic gauze in the following manner: Strips of gauze 2 in. wide and about 15 in. long are dipped in the paint for about 13 in., then drawn through a wringer consisting of two test tubes ($\frac{1}{2}$ by 6 in.) drawn together by elastic bands. Gauze having these dimensions weighs about 1.25 grams. The weight of each piece of gauze is previously obtained, and after it has been dipped in the paint it is placed on a clock glass. The clock glass and its contents are then weighed, from which, by deducting the weight of the clock glass and any adhering paint, we obtain the amount of paint which has been placed on the gauze. This gauze is then hung up to dry for about ten days with a tared clock glass under it, so that paint drippings may be caught and weighed and deducted from the amount of paint taken. After ten days the gauze and paint are weighed, and if desired the percentage gain in weight may be calculated. The painted gauze is then placed in a 150 c.c. beaker and covered with about 130 c.c. of distilled water. After 24 hours this water is poured off and evaporated and another 130 c.c. of water is placed on the gauze. The water poured off is placed in a tarred vessel, so that after evaporation to dryness the amount dissolved can be determined by weighing. This dissolved matter can then be analyzed for pigment constituents or treated with nitric acid, and carefully ignited and weighed. The treatment with water can be repeated as often as may be desirable, and, if it is thought best, the extract from several treatments can be combined and

¹ G. W. Thompson. Certain Solubility Tests on Protective Coatings. Proc. Amer. Soc. Testing Materials, 1908, Vol. VIII, p. 601.

treated as one." The results obtained by this test have brought out some interesting points. It has shown, for instance, that in paints compounded of different pigments, some of these may be dissolved out by the action of water. As a specific instance of this, the case of Venetian red may be cited, which contains a large percentage of calcium sulphate. Such a pigment would prove dangerous to use on iron or steel, on account of the solubility of the calcium sulphate.

The tables previously presented in this chapter, in which is given the list of inhibitive pigments, and also the list of excluding pigments, should prove of great value to the manufacturer in aiding him to select the best materials for the composition of paints for the protection of iron, and it is hoped that the tests described will be given full consideration in conjunction with the more practical field tests which are now being conducted.

The architect and the engineer are constantly clamoring for protection for the enormous structural work under their supervision. More attention than ever is being paid to recent investigations on the subject of paints, and better materials for painting purposes are being insisted on. It is fair to believe that those in charge of engineering work will demand in the future vital improvements in steel protecting compounds, based on modern knowledge of the problem. As has been previously pointed out, the day of empiricism in the selection of protective coatings has passed, and the subject must now be considered from the standpoint of scientific investigation based upon a satisfactory working theory. The treatment of steel surfaces by the metallurgist, either by physical or chemical means, may soon be developed to such an extent that metal will be made almost non-corrodible, but until such a day comes there will be an immense demand for protective coatings that will protect, and too much attention and study cannot be given to the subject.

CHAPTER VIII

RECENT FIELD TESTS ON PROTECTIVE COATINGS FOR IRON AND STEEL

Steel Test Panels at Atlantic City. — The results obtained by recent investigators on the inhibitive value of pigments, as described in the previous chapter, suggested the erection of a series of steel panels on which could be tested the same range of pigments under the practical conditions of service in the open. The Paint Manufacturers Association of the United States offered to erect the panels, and place them under the supervision and inspection of Committee "U" of the American Society for Testing Materials. It was decided to erect the panels near Atlantic City, N. J., and the work was commenced during the fall of 1908, at this place. In order to broaden the test, and furnish data in regard to the durability of the various paint films when placed on different types of metal, three kinds of steel were used on the panels.

The following table shows the analyses of the three grades of metal tested:

	Bessemer	Open Hearth	Extra Mild Open Hearth
Carbon08	.16	.03
Phosphorus08	.02	.005
Sulphur05	.024	.024
Manganese35	.44	trace only

Pickling and Preparation of Plates. — The three types of metal selected for the test were rolled to billets, the middle of which were selected, and worked up into plates 24 in. wide, 36 in. high, and $\frac{1}{8}$ in. in diameter — approximately 11 gauge. A number of plates of each of the metals selected, in all 450, were pickled in 10 per cent. sulphuric acid, kept at 180 to 200° F., in order to remove the mill-scale. The plates were then washed in water, and later in a 10 per cent. solution of caustic soda. Finally the plates were again washed in water and wiped dry. They were

¹This metal is called "Ingot Iron" by the manufacturers.

then packed in boxes containing dry lime, in order to prevent superficial corrosion. By this method the plates were secured in perfect condition, the surfaces being smooth and free from scale. Upon these pickled plates, paints were applied with a definite spreading rate of 900 sq. ft. per gallon. The unpickled plates, coated with mill-scale, were painted with the same paints, but without adopting any special spreading rate, thus following more closely the ordinary method of painting structural steel. A few extra plates of special Bessemer steel and Swedish charcoal iron were also included in the test, some of which were painted, while others were exposed without any protective coating. Plates of the three types of metal already mentioned were also exposed unpainted, both in the black and pickled condition.

Fence Erection and Preparation for Work. — The fences which were erected for the holding of the plates were constructed of yellow pine, the posts being set deeply in the ground and properly braced. The framework of the fence was open, with a ledge upon the lateral girders, upon which the plates might rest, and to which the plates were secured by the use of steel buttons. After the framework had been erected, painted, and made ready for the placement of the panels, a small shed was built upon the ground, and the materials for the field test placed therein. The steel plates were unpacked from the boxes in which they were shipped, brushed off, and stacked up ready for painting. Small benches were erected, and the accessories of the work, such as cans, brushes, pots, balances, etc., were placed in position.

Method Followed in Painting Plates. — A frame resting upon the work bench served to hold the plates in a lateral position while being painted, room being allowed beneath the plate for the operator to place his hands in order to lift the plates from the under surface, after the painting had been finished.

A pickled plate having been placed upon the framework, everything was in readiness for the work. The specific gravity and weight per gallon of the paint to be applied was determined, and the amount, in grams, to be applied to each individual panel was calculated according to the following formula:

$$\begin{array}{ccccccc} \text{Spreading rate} & \text{sq. ft. in plate} & & \text{grams paint in gal.} & & & \\ 900 \text{ sq. ft.} & : & 6 & : : & 4500 & : & x \end{array}$$

The reciprocal of x being the number of grams of paint to be applied to the panel.

An enamel cup was then filled with the paint and a brush well stirred within. The cup, paint, and brush were placed upon the balances and accurately weighed in grams. After most of the paint had been applied to the panel, cross-brushing of the panel was continued until the pot with brush and paint exactly counterbalanced the deducted weight. The painted panel was then set in a rack, in a horizontal position, to dry.

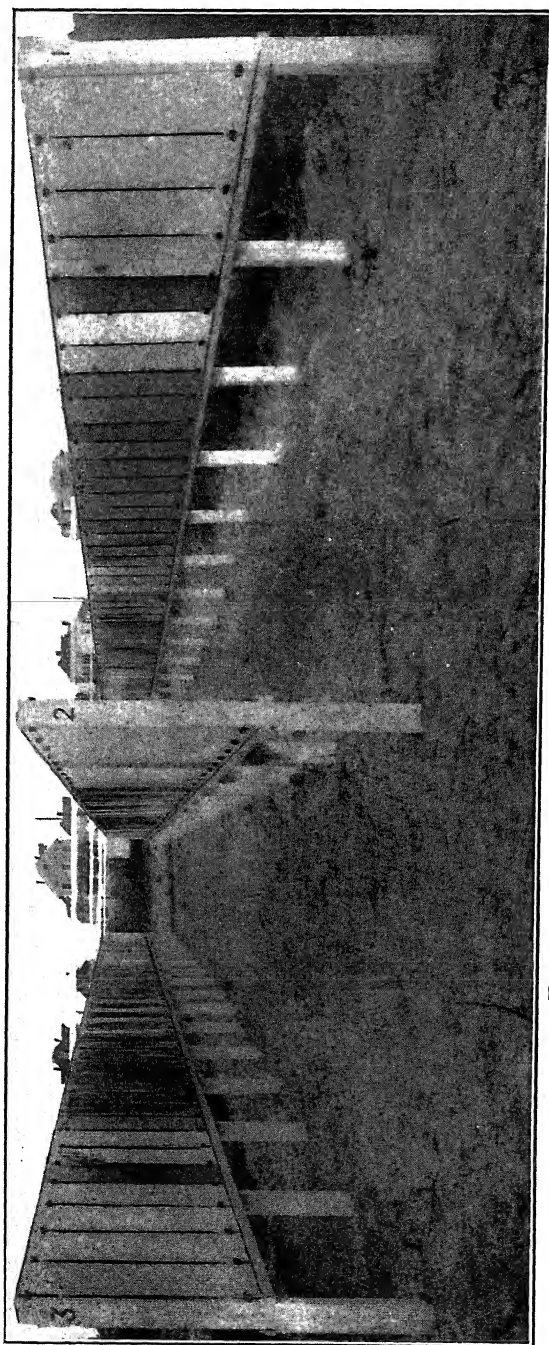
A period of eight days elapsed between the drying of each coat. The greatest care was taken in the painting of the edges of the plates, and the racks for containing the plates after they were painted were so constructed that the paint would not be abraded while sliding the plates back and forth. The working properties of each paint, and the appearance of the surface of each plate after painting were carefully noted and included in the report. No reductions were made to any of the paints applied except in three cases, where the viscosity was so great that it was necessary to add a small amount of pure spirits of turpentine. The amount of paint was proportionately increased in such cases, so that the evaporation of the turpentine would leave upon the plate the amount of paint originally intended.

The appearance of the completed series of test panels is shown in Fig. 41.

Vehicles Used and Reasons for Avoidance of Japan Driers. — The pigments used were selected with the view to securing as nearly as possible purity and strength, and as already noted were out of the same lots used in making the preliminary laboratory tests on inhibitives. They were ground in a vehicle composed of two parts of raw linseed oil and one part of pure boiled oil. Paint is generally caused to dry rapidly by the use of japans or driers. These materials contain a large amount of metallic oxides which might have some effect in either exciting or retarding corrosion. To prevent the introduction of such a factor, these materials were not used in the test. The boiled oil, with its small percentage of metallic oxides, was sufficient, however, to cause the paints to dry in a short time after they were spread.

The table on page 184 gives the number of pounds of pigment to a gallon of oil, used in the manufacture of the pigment paints for this test. The formula for determining the amount is as follows:

$$\text{Sp. Gr. of pigment} \times 3 = \text{lbs. pigment to gal. oil}$$



• FIG. 41. — Completed Steel Test Panels at Atlantic City, N. J.

The excessive amount of oil required to grind pigments Nos. 19 and 21 made it necessary to introduce a percentage of barytes (barytes requiring very little oil), in order to form paints which would contain relative amounts of oil.

Pig- ment No.	Name	Sp. Gr. of Pigment	Weight of Pigment to Gal. Oil	Weight of Paint per Gal.
			<i>Lbs.</i>	<i>Lbs.</i>
1	Dutch Process White Lead	6.83	20.49	20.4
2	Quick " " "	6.78	20.34	20.56
3	Zinc Oxide	5.56	16.68	17.68
4	Sublimed White Lead	6.45	19.17	19.65
5	" Blue Lead	6.39	19.17	20.1
6	Lithopone	4.26	12.78	15
7	Zinc Lead White	4.42	13.26	16.37
9	American Orange Mineral	8.97	26.91	24.74
10	Red Lead	8.70	26.10	24.4
12	Bright Red Oxide	5.26	15.78	17.07
14	Venetian Red	3.1	9.30	12.6
15	Prince's Metallic Brown	3.17	9.51	12.49
16	Natural Graphite	2.60	7.80	11.4
17	Acheson Graphite	2.21	6.63	10.2
19	{ Lampblack	1.82	1.82	{ 13.32
	{ Barytes		8.92	
20	Willow Charcoal	1.49	4.47	8.99
21	{ Gas Carbon Black	1.85	1.39	{ 13.94
	{ Natural Barytes		10.03	
24	French Yellow Ochre	2.94	8.82	12.16
27	Natural Barytes	4.46	13.38	15.24
28	Precipitated Barytes (Blanc Fixe) . .	4.23	12.69	15.32
29	Calcium Carbonate (Whiting)	5.48	8.22	11.41
30	Calcium Carbonate Precipitated . . .	2.56	7.68	11.24
31	Calcium Sulphate (Gypsum)	2.33	6.99	10.41
32	China Clay (Kaolin)	2.67	8.01	11.19
33	Asbestine (Silicate of Magnesium) . .	2.75	8.25	11.49
34	American Vermilion (Chrome Scarlet)	6.83	20.49	21.36
36	Medium Chrome Yellow	5.88	17.64	18.8
39	Zinc Chromate	3.57	10.71	13.07
40	Zinc and Barium Chromate	3.45	10.35	13.16
41	Chrome Green (Blue tone)	4.44	13.32	16.16
44	Prussian Blue (Stimulative)	1.96	5.88	9.95
45	Prussian Blue (Inhibitive)	1.93	5.79	9.76
48	Ultramarine Blue	2.40	7.20	10.74
49	Zinc and Lead Chromate	4.76	14.28	15.99
51	Magnetic Black Oxide		15	15.99

NOTE. — The oil used in grinding all these pigments and used throughout the test was composed of two parts raw linseed oil and one part boiled linseed oil. The specific gravity of this mixture was .937.

Data of application of each pigment was accurately made during the tests. There is given herewith the data on four of the pigments applied.

No. 2, Quick Process White Lead:

Sp. Gr. of Pigment	6.78
Lbs. to Gallon Oil	20.34
Sp. Gr. of Paint as Received.....	2.47
Wt. of Paint per Gallon	20.56
Grams to Panel	62
Condition of Paint	Good
Working Properties.....	Works easy
Drying	24 hours all coats
1 Coat Oct. 26 T 60 B 29.94 W fair	
2 Coat Nov. 3 T 54 B 30.23 W clear	
3 Coat Nov. 7 T 52 B 29.66 W cloudy	

No. 9, Orange Mineral (American):

Sp. Gr. of Pigment.....	8.97
Lbs. to Gallon Oil	26.91
Sp. Gr. of Paint as Received...	2.97
Wt. of Paint per Gallon	24.74
Grams to Panel	74.7
Condition of Paint	Good
Working Properties	Smooth — no brush marks.
Drying	Good
1 Coat Oct. 28 T 58 B 30.01 W cloudy	
2 Coat Nov. 4 T 65 B 29.61 W cloudy	
3 Coat Nov. 9 T 58 B 29.91 W clear	

No. 14, Venetian Red:

Sp. Gr. of Pigment.....	3.1
Pigment to Gal. Oil	9.30
Sp. Gr. of Paints Received	1.52
Wt. of Gallon Paint	12.6
Grams to Panel	38
Condition	Good Smooth Paint
Working Properties.....	Smooth — no brush marks.
Drying	Good on all coats
1 Coat Oct. 29 T 56 B 29.82 W cloudy	
2 Coat Nov. 4 T 65 B 29.61 W cloudy	
3 Coat Nov. 9 T 65 B 29.91 W clear	



No. 19, Lampblack:

Sp. Gr. of Pigment	1.82
Lbs. to Gallon Oil: Lampblack ...	1.82
Barytes	8.92
Sp. Gr. of Paint as Received	1.60
Wt. per Gallon Paint	13.32
Grams to Panel	40.2
Condition	Good
Working Properties	Works fair
Drying	Slow. Tacky after 3 days.

1 Coat	Oct. 29	T 56	B 29.82	W cloudy
2 Coat	Nov. 5	T 54	B 29.92	W clear
3 Coat	Nov. 10	T 60	B 30.02	W clear

NOTE. — T stands for temperature (F)
 B “ “ barometer
 W “ “ weather

Testing Effect of Various Prime Coats. — Some of the special tests made, included a series of plates prime-coated with different inhibitive pigments, and these tests were designed to determine which pigments offer the best results for such work. These plates were all second-coated with the same paint. It is the opinion of the authors that any good excluding paint may be used whether it is inhibitive in action or not, provided the contact coat is inhibitive. If, however, both coats can be designed so as to have the maximum possible value from both these points of view, the best results would, of course, accrue. The only way such data can be obtained is by careful observation of the results of exposure tests.

Combination Formulas Tested. — By selecting a series of pigments which in the water tests showed inhibitive tendencies, and properly combining these pigments into a paint, it was thought possible that a more or less inhibitive paint would be produced. If this proved to be the case, it would follow that the selection and introduction into a paint of the stimulative pigments would inevitably produce a paint unfit for use on iron or steel. Formulæ of both types were therefore used in these tests, and below the percentage composition of two of these is shown.

INHIBITIVE WHITE.

Pigment Formula		Paint Formula
35 per cent.	Zinc Oxide	20.90 per cent.
45 per cent.	Special White	26.87 per cent.
5 per cent.	CaCO ₃	2.98 per cent.
15 per cent.	Silex	8.95 per cent.
	Japan	1.56 per cent.
	Raw Oil	38.74 per cent.

STIMULATIVE BLACK.

Pigment Formula		Paint Formula
40 per cent.	Lampblack	8.18 per cent.
40 per cent.	Natural Graphite ..	8.18 per cent.
20 per cent.	Barytes	4.09 per cent.
	Japan	8.33 per cent.
	Raw Oil	71.22 per cent.

Drawing Conclusions from Results of Field Tests.—At the present writing, the Atlantic City test plates have been in place fourteen months, and the authors do not consider that sufficient time has elapsed to justify definite conclusions or sweeping deductions. In a number of cases, however, the panels have actually failed, and the corrosion effects are apparent to all observers. The authors fully recognize and desire to record here that in spite of the fact that they were the principal responsible persons in charge of the design and erection of these tests, nevertheless, in view of the fact that no official report of results obtained has yet been made to the American Society for Testing Materials, it would not be proper to enter upon a discussion of the relative durability of the different types of formulæ, even if definite results had begun to show.

It is, however, fair to record the results of scientific examinations of the paint surfaces, which have been made from time to time, leaving the conclusions which will naturally follow from these observations to be drawn later. The object of the authors in presenting a detailed description of the design and construction of these fences has been solely to act as a guide for other experimenters who may desire at some future time either to duplicate or develop this form of field testing. It is by no means easy to carry out work of this kind which involves a very large amount of thought and labor. The experience gained by one set of experimenters will, of course, prove valuable to others who are pursuing the same line of research.

The Inspection of Painted Surfaces. — In making an inspection of painted surfaces to determine the durability of various coatings, the chalking, checking, color, maintenance, elasticity of film, and other properties should be noted.

By the term chalking is meant that condition of the film which allows removal of the pigment when rubbed with the hands or with cloth pads. Destruction of the oil, through the saponification caused by alkaline pigments, is often the primary cause of chalking.

By checking is meant that condition of the painted surface that shows checks, cracks, alligatoring (an appearance resembling alligator skin), etc. Checking may be seen very clearly by using a small but powerful magnifying glass. Surface, matt, coarse and deep are qualifying terms used to define the character of the checking which takes place. Paints which are not elastic and which become brittle are subject to checking, as well as some paints which chalk readily.

Elasticity of film is noted by raising a portion of the film with the knife blade and peeling it off. Only very elastic paint will stand this test. Brittle coatings crumble up at once when this attempt is made. This test cannot, of course, be applied to the Atlantic City panels, but is in general use by car painters.

Hardness of coating can be gauged to a certain extent by the appearance of the paint film and its resistance to abrasion. A small hard object is sometimes used to strike against the painted surface to determine its hardness. The hiding power and color maintenance of paints are also important features to consider in making an inspection.

Continuity of coating and absence of disintegration, as well as other conditions of the paint film, is best determined by examination with a microscope. This can be done by using the photomicroscope designed by one of the authors. This apparatus has proved of great value in field inspection work. Permanent records of the wearing of a paint from time to time can be obtained by using this instrument, and the progressive decay shown, determined with accuracy.

The photomicroscope consists of a modified form of a Gordon photomicrographic tube such as is used for plate exposures in laboratory work. This tube contains a projection lens properly focused, and also an exposure shutter fixed on a lift pin. On the

rear end of the tube is fitted a disk of metal, into which is placed a block of wood having a central annular opening the size of the tube. On the back of the wood is firmly set and screwed into position a film-pack holder, such as is used for the ordinary photographic camera. The arm and body of a microscope, containing a draw tube fitted with objective and eye-piece, is mounted in a horizontal position on a solid iron base, bored and threaded to receive a screw from the top of a heavy tripod. The objective of the microscope is placed close to the painted surface, and by raising or lower-

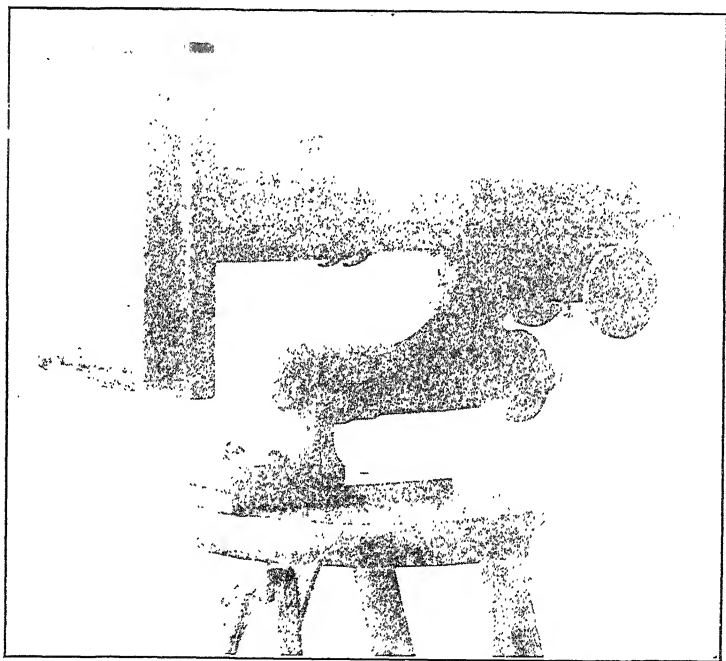


FIG. 42. — Photomicroscope for examining and photographing painted surfaces. (Gardner.)

ing the tripod the microscope may be focused on any spot, by the regulation of the coarse adjustment. Minute abrasions or cracking of any nature can easily be detected. When all is ready, the tube camera is placed directly over the eye-piece of the microscope, and exposure is made by lifting the shutter cap for twenty or thirty seconds, according to the light conditions. No artificial illumination is necessary. The apparatus is shown in Fig. 42.

In using the photomicroscope on the Atlantic City panels, one of the first effects shown was the appearance of minute crystals of sodium chloride deposited on the films from the saline atmosphere due to the close proximity of the ocean.

A very interesting point brought out by these examinations is the fact that some of the paint films appeared to have the power of holding the salt crystals to a much greater degree than others, some, indeed, being almost free from salt. A sufficient amount of work has not yet been done along this line to enable definite conclusions to be drawn, but some of the results obtained are shown in order to stimulate further inquiry. In Figs. 43 a, b, and c are shown photomicrographs of three different paint coatings, to illustrate this point.

The tendency of certain paint coatings to produce a slight wrinkling of the surface when softened by moisture is well known. This action, which is probably preliminary to a breaking down of the paint film, is shown in Fig. 44.

As has been pointed out in a previous paragraph, certain pigments rapidly destroy the oil films and produce the phenomenon known as chalking. The appearance of chalked paint films is very characteristic under the photomicroscope. The effect is very well shown by Figs. 45 and 46.

The cracking of paint films is a most important point in relation to the general subject of the protection of iron and steel by paint coatings. It requires no evidence to prove that the opening up of cracks on the surface will allow water, and the other corroding influences, to make a ready entrance to the surface of the metal, and act as centers of corrosion.

The photomicrographic method of studying paint films will undoubtedly lead to more definite information on this point than has been heretofore available. A study of the illustrations, as shown in Figs. 47, 48, and 49, indicates that cracks in different paint coatings are of a different nature and appearance.

It is well known that although zinc oxide has many properties which make it an extremely valuable pigmentary substance, its tendency to crack constitutes its greatest fault. The cracking of a zinc oxide film is beautifully illustrated in Fig. 47. Another peculiar form of cracking is shown in Fig. 49 on a gypsum coating.

Other types of cracking which are being closely followed by corrosion along the line of the cracks are shown in Figs. 50, 51, 52.

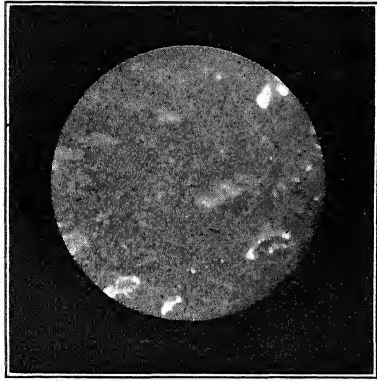


FIG. 43 (a). — Crystals of sodium chloride deposited from saline atmosphere upon iron oxide coated panel.

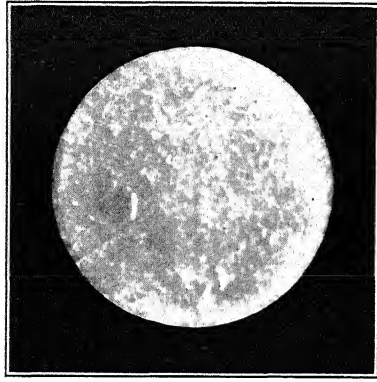


FIG. 43(b). — Fine crystals of salt on asbestos panel.

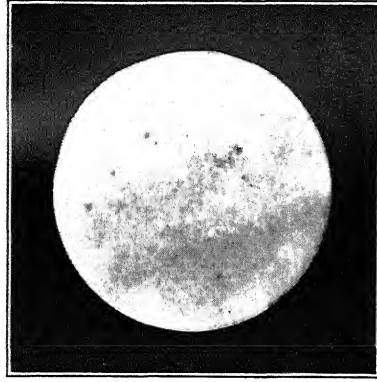


FIG. 43 (c). — Paint coating composed of zinc oxide, lead sulphate, and silica, showing no salt crystals.

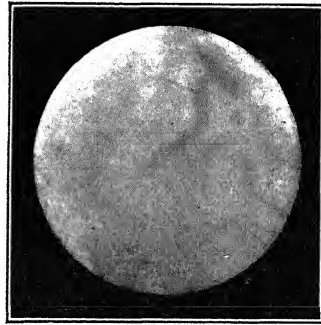


FIG. 44. — Slight wrinkling of paint coating softened by moisture.

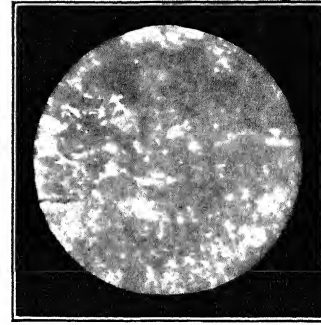


FIG. 45. — Photomicrograph of calcium carbonate. Excessive chalking has caused vehicle decay and rough surface.

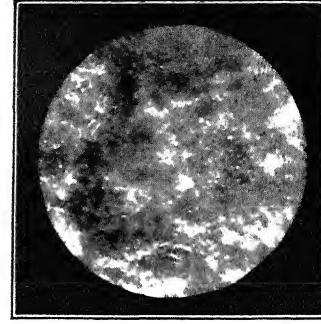


FIG. 46. — Photomicrograph of gypsum showing strata of rust under rough surface caused by disintegration and washing of pigment.

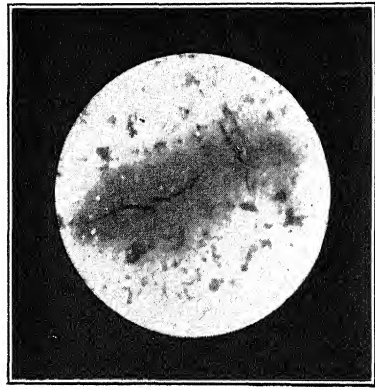


FIG. 47. — Cracked coating of zinc oxide.

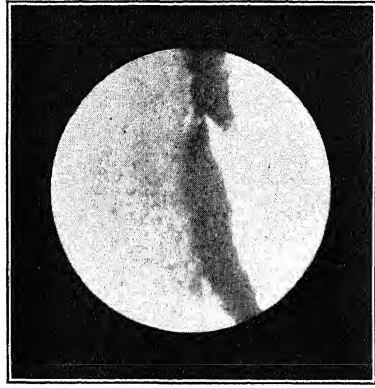


FIG. 48. — Cracking in barytes film and subsequent corrosion showing through.

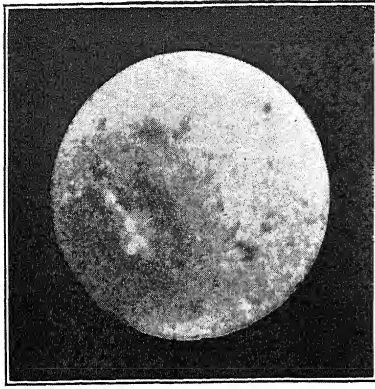


FIG. 49. — Corrosion on line and crack on gypsum.



FIG. 50. — Peculiar cracking followed by rust spots on white lead.

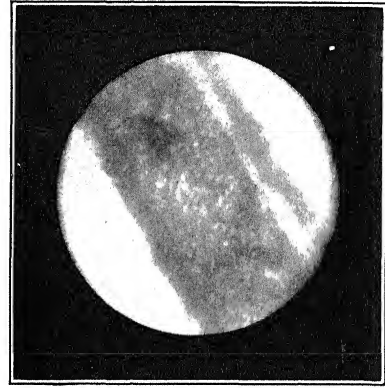


FIG. 51. — Broad cracks in brittle paint coatings.

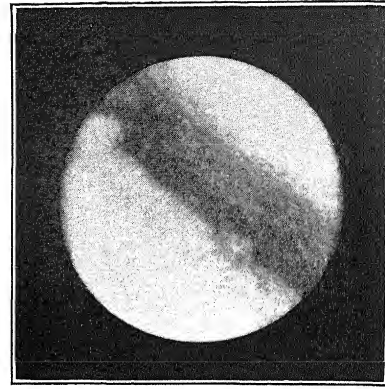


FIG. 52. — Corrosion proceeding from cracks and appearing under surface.

The recent work of Walker, calling attention to the probability that cracks in paint films are responsible for a stimulated corrosion effect owing to the depolarizing action of the open paint film, due to the absorption of nascent hydrogen, is particularly interesting when considered in relation to the effects shown in these illustrations.

On Figs. 53 and 54 are shown two typical examples of checking. This action, just as in the case of cracking, must be considered a preliminary step in the breaking down of a paint coat, leading to corrosion. Fig. 55 illustrates the effect produced by uneven brush work, leading to a special characteristic form of checking which is frequently observed as a preliminary step in the breaking down of paint coatings.

Figs. 56, 57, 58 exhibit in a very interesting manner the breaking through of corrosion nuclei to the surface of the paint film. It must be apparent that although a paint film may be opaque, corrosion goes on underneath for a long time before the trouble becomes evident on the surface. A time comes, however, when little blisters make their appearance on the film. This appearance is a preliminary step to the breaking out of the tubercles of rust which are so familiar to all observers.

The rusting of iron has frequently been compared to a malady or disease, and certainly these photomicrographs appear to show a striking analogy with the effects produced by disease in living tissue.

The authors have stated in a previous paragraph that it is perfectly fair for every observer to call attention to specific cases of success or failure exhibited by the Atlantic City test panels, provided no sweeping conclusions are reached or deductions drawn. While bearing this in mind, it serves our purpose to present herewith some illustrations representing interesting contrasts which the tests have already served to show. The authors do not hesitate to appear as defenders of the electrolytic theory of corrosion, and therefore of the value in general of inhibitive pigments. Fig. 59 illustrates the condition of a plate painted with zinc chromate, a distinctly inhibitive pigment.

Fig. 60 shows the present condition of two plates painted respectively with pigments, one of which is a distinct stimulator of corrosion and the other of which saponifies and destroys the protective film. An inspection of this illustration shows that

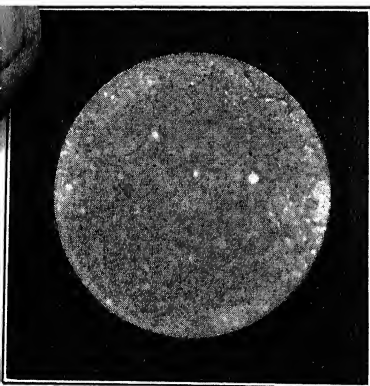


FIG. 53. — Checking on ultramarine blue.

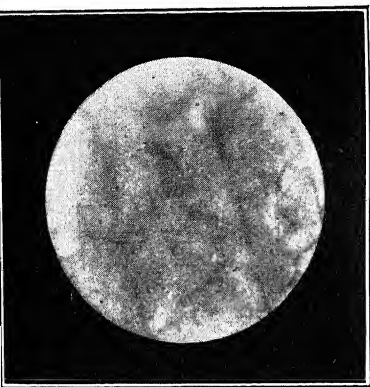


FIG. 54. — Checking of painted surfaces.

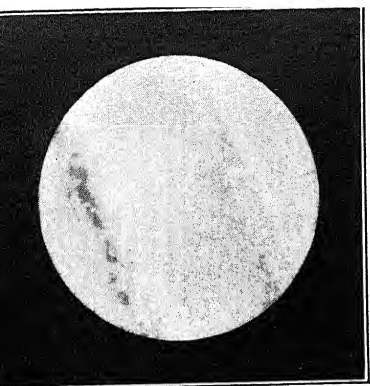


FIG. 55. — Brush marks on paint applied too thick. Thick places liable to break down.

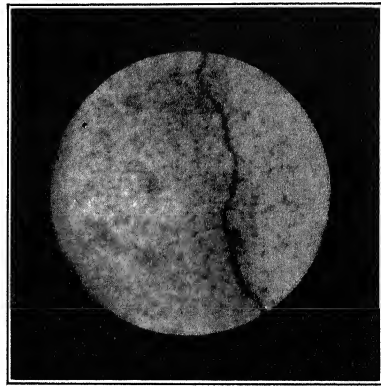


FIG. 56. — Rust exudation on painted panel.

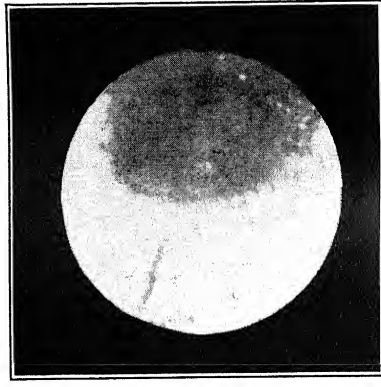


FIG. 57. — Nodule of rust appearing through paint film.

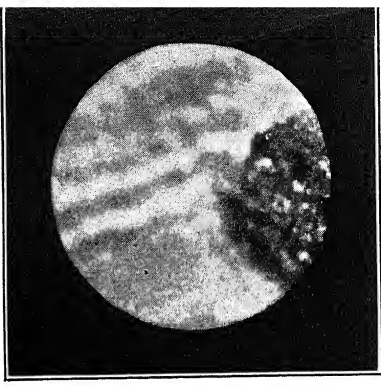


FIG. 58. — Cracking in paint coating. Probably caused by rust spots due to segregated manganese sulphide in metal.

the plate painted with the gypsum is dark in color. This darkness is due entirely to the corrosion which is plainly seen to be taking place underneath the more or less transparent film. That this same action is going on under many of the opaque films can hardly be doubted, although it is not at the present time apparent to the eye.

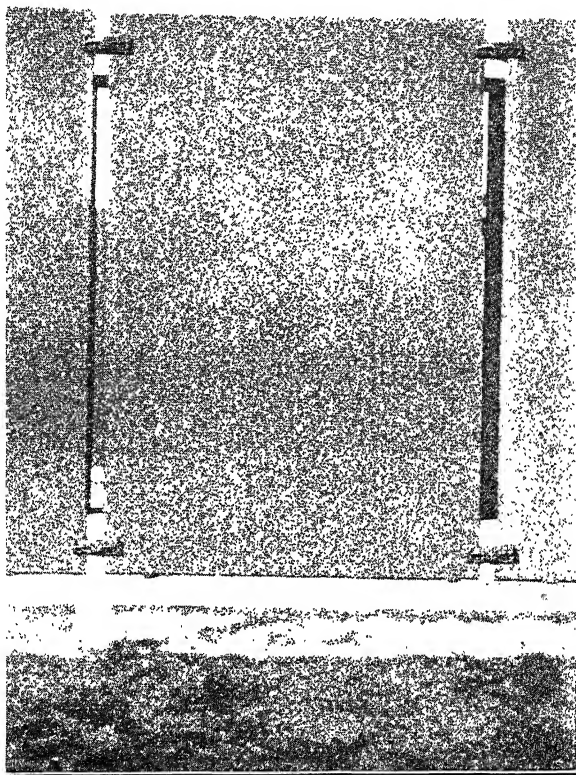


FIG. 59. — Perfect condition of plates painted with zinc chromate.

It is well known that calcium carbonate as a pigmentary substance is used in two different forms — the natural, ground chalk (or whiting), and the precipitated calcium carbonate. In view of the fact that calcium carbonate is a useful ingredient in small percentage in many paint formulæ, it is interesting to

record the condition of the two plates which have served as a test of the relative value of these two forms. An inspection of Fig. 61, taken in conjunction with Fig. 62, in the same plate, appears to indicate that the whiting or natural form of calcium carbonate should be selected, if it must be used, for all protective paints for iron.

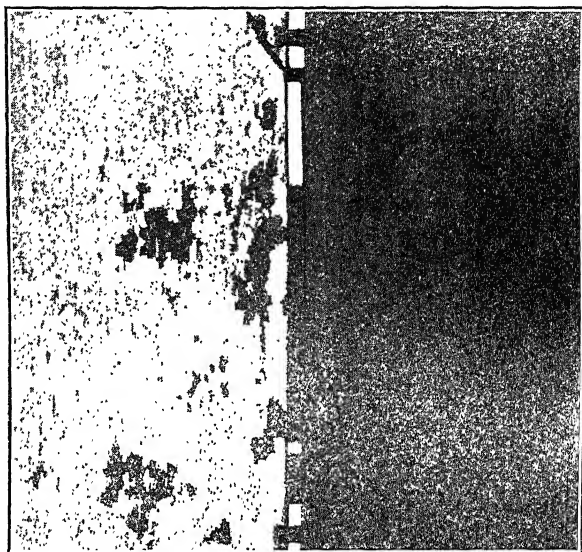


FIG. 60. — On left, scaling and corrosion on plate painted with precipitated calcium carbonate. On right, corrosion showing through gypsum paint film.

Other Field Tests and their Value. — J. Cruickshank Smith,¹ in commenting on paints for the preservation of steel, makes an appeal for more field tests such as those already described, in the following words: "Although opinions vary as to what is theoretically the best pigment, or, more correctly, combination of pigments, for the manufacture of protective coatings, the general consensus of technical opinion seems to be gradually coming to be that, with certain more or less obvious reservations, the com-

¹ A Plea for International Investigation concerning Protective Coatings for Iron and Steel. Paper submitted to 5th Congress, Internat. Assn. for Testing Materials, Copenhagen, 1909.

position of the paint is less important than its physical state, and that one pigment or blend of pigments is more efficient than another as the basis for a protective paint mainly according to the degree in which it tends to produce certain definite physical and mechanical effects in the ultimate protective film. The problem that remains is the selection of that blend of pigments,

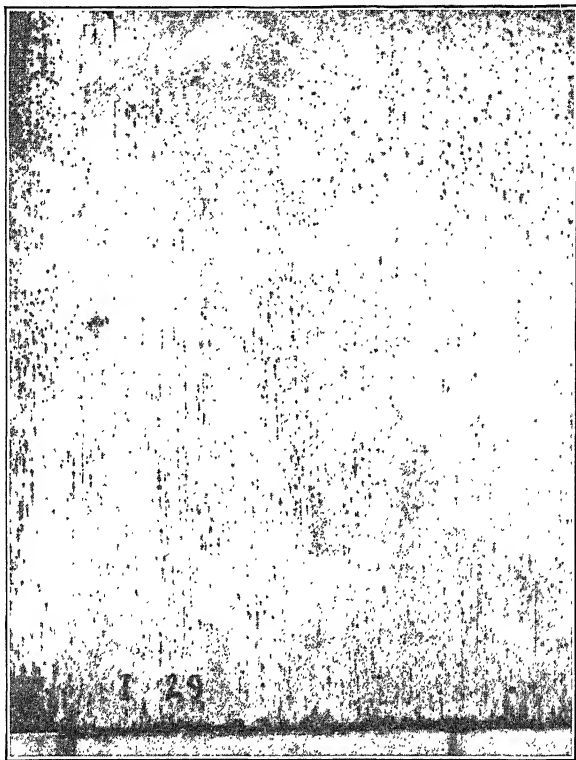


FIG. 61. — Whiting (calcium carbonate) on steel.

suspended in a suitably adjusted vehicle (the paint as a whole possessing the necessary physical properties), which will, under known conditions as to exposure and climatic conditions, yield a satisfactory protective film. Only exposure tests can solve this problem.

“It is now generally accepted that such factors as fine state of division and uniformity in size of the pigmentary particles, viscosity of the paint, elasticity and strength of the paint film,

and impermeability of the paint film to moisture and gases, are of paramount importance in determining whether or not a particular paint will satisfactorily effect the purpose of a protective coating. In this connection, I would direct attention to the admirable scientific work recently accomplished, and still being conducted by the Scientific Section of the Paint Manufacturers'

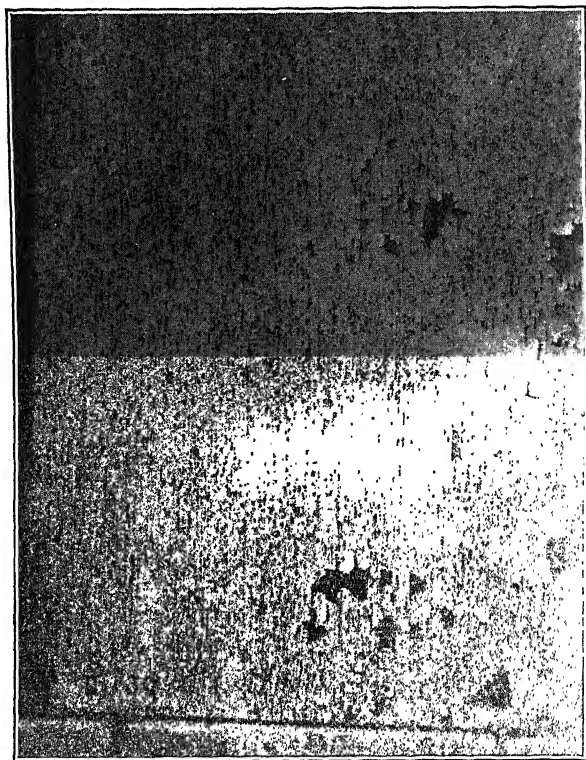


FIG. 62. — Precipitated calcium carbonate on steel.

Association of the United States, and also by the various committees of the American Society for Testing Materials. The official publications of these two bodies teem with technical matter, which no one who claims to be up-to-date in his knowledge of this subject can afford to be ignorant of."

Another practical service test of paint is being carried on by Committee "E" of the American Society for Testing Materials on a Pennsylvania Railroad bridge at Havre de Grace, Mary-

land.¹ In this test a number of protective paints, selected from those largely advertised in the American market, were used. The following outline of the tests will be of interest to the engineer and bridge builder, who have the protection of similar structures under their supervision.

Tests on Preservative Coatings Carried on under the Supervision of Committee "E," American Society for Testing Materials.

"1st. — Actual Service Tests under Normal Conditions to be Applied to Full-Size Structures and Normal Panel Tests.

"Under this head the Committee started a long-time service test in June, 1906, on part of the new double-track deck bridge of the Pennsylvania Railroad over the Susquehanna River, at Havre de Grace, Maryland. The bridge is about 4000 feet long, consisting of 16 spans. The trusses are 30 feet deep, and the panels 29 feet long. The paint was supplied by 19 manufacturers, and applied to 2 continuous spans of the bridge directly over the water, containing 19 panels. Each panel represented one paint test.

"In addition to the test of the paint on the bridge proper, panel tests were also made on very carefully prepared steel plates, 2 feet by 3 feet, the paint being applied by a most skilful workman, under the most perfect conditions possible. These panels were made in triplicate at 3 spreading rates, 600, 900, and 1200 square feet per gallon of paint. The panels are exposed on the lower chord of the bridge.

"Conditions of surface, application, weather, etc., were carefully noted and recorded. Complete analyses of the paints used in the test were made. The paints used in this tests were, in most cases, the representative proprietary coatings prepared for use on iron and steel structures.

"The pigments included red lead, graphite, carbon, oxide of iron, white lead, zinc oxide, sulphate of lead, together with clay, silica, silicate and barytes. The oil was in the majority of cases a pure linseed oil, though in one case rosin or a resinat drier was detected.

"The volatile matter was found to be turpentine or naphtha, or a mixture of the two.

¹ Résumé of Work done by the American Society for Testing Materials on Preservative Coatings for Iron and Steel, presented at the Annual Meeting of the International Society, September, 1909.

"In the set was one heavy asphaltic varnish thinned with naphtha.

"The result of the inspection made in June, 1908, is as follows:

"As was anticipated, no marked differences are noted in the majority of cases. As was clearly indicated at the inspection a year ago, the only example of an asphaltum varnish thinned with a petroleum solvent has failed to a marked degree after eighteen months' exposure. A carbon paint containing rosin in the oil has developed minute fissure cracks all over the surface. While it is by no means conclusive that this failure is due to the rosin, still it is worthy of note, and will be the subject of further investigation.

"An example of difference of expansion of red lead under-coat and a carbon final-coat is shown in panel 14. The carbon coat has cracked badly on the bridge proper in cobweb-like cracks, showing the red of the under-coat. On another panel the same final-coat, however, applied both as an under-coat and as a final-coat, has not failed in this manner.

"It is also interesting to note that one of the pure red lead pigments in straight raw linseed oil shows unmistakable evidence of alligatoring.

"High gloss and tenacious film are shown by Panel 1. In this case the pigment consists of oxide of iron, red lead, and a carbon black, mixed with a varnish containing some gum and thinned with turpentine.

"The other panels, as stated in the report of the sub-committee, show in most cases a marked loss of gloss with minor differences in hardness, tenacity, toughness, and elasticity of film. These differences are, however, too slight to warrant an opinion at this time.

"There is evidence of rusting to a slight degree on all sections of the bridge, due to mechanical injury. These spots have been accurately noted and will be carefully watched at subsequent inspections. In general, however, the paints are affording good protection, and it will require longer exposure to differentiate in the majority of cases.

"An inspection made March 26, 1909, confirms the report of last June, with no marked changes of note to report. As stated in June, one of the red leads showed unmistakable evidence of alligatoring. At the inspection just made, the other sample of

red lead shows the same condition though to a less marked degree. In both cases the alligatoring is most marked at the spreading rate of 600 square feet to the gallon, but the cracking is apparently superficial. Good protection is afforded, however, by both paints.

"In general, most of the paints are affording good protection.

"It is impossible to give details of the tests in this paper, but reference is made to reports of Committee 'E' in Proceedings of the American Society for 1906, 1907, and 1908."

Considering the fact that nearly all these paint coatings are reported to be in fairly good condition after about four years' exposure, it would appear that the conditions of service at this place are by no means severe. All the panels and sections are located far down on the bridge structure where they cannot come into direct contact with sulphurous gases from the locomotives. It is more than probable that in some other location more definite results of the tests would have been obtained in the time elapsed.

Tests of Paint Coatings Designed to Resist Sea Air.—The attack of sea-water and a saline atmosphere upon paint coatings is very severe. The soluble salts which are constituents of sea water have the power of penetrating the hardest paint coatings known, and acting to a certain extent the part of paint removers. In the opinion of the authors, it is extremely important that the paint designed to protect metal exposed to sea-water and sea-air should contain inhibitive pigments. If such paints contain pigments which are stimulative in nature, it is logical to assume that in the presence of such easily ionized salts as the sea-water contains, energetic galvanic action might proceed, with subsequent rapid pitting and corrosion. Moreover, the necessity of an extremely good excluding vehicle for paints, designed for the protection of marine structures, has been demonstrated by many tests.

Along the various resorts on the New Jersey coast, thousands of examples of the rapid decay of paint coatings applied to structural metal may be seen. On some of the old steel piers which extend out to the ocean, ordinary coatings which have been renewed almost yearly are in many cases destroyed after a few months' exposure. The girders under the board walks, and the railings above them, offer striking examples of the fugitive nature of the ordinary paint coating when exposed to the action of salt

spray and salt air. Steel must be used in some places where the use of concrete is not applicable, or where the present state of development of the art of erecting concrete structural material has not reached the necessary perfection. A combination of steel and concrete would probably prove the solution of many of the engineering problems at present met with, but the demand for an efficient paint to withstand salt exposure is as great as ever, and the tests which are under way may provide a solution of the difficulty. The management of Young's Old Pier, at Atlantic City, working in conjunction with the Carnegie Steel Company, have recently erected a series of columns or piles on the beach, under the supervision of one of the authors, in order to determine the resistance to corrosion, and permanence of a combination of one of the carefully designed types of modern steel and cement construction. The test consists of a series of five piers about 18 in. in diameter. The piers are made of steel sheet piling locked together, filled with concrete, and sunk to two thirds their depth in the sand, so that at low tide one third of the height of the piling is subjected to the action of the salt air, while at high tide the piling is completely covered. Details of construction are shown in Fig. 63. Previous to assembling and erecting this piling, the steel parts were all carefully painted with different paint formulæ to determine which was best suited for the purpose. The rise and fall of the tide, with the constant swirl of the sand in its grasp, causes an enormous and unusual abrasion effect on the paint coating, while the alternate exposure to the disintegrating effect of the salt water and the oxidizing effect of the air offers one of the most severe tests to which a paint could be put.

On the ocean end of Young's Old Pier, at Atlantic City, the United States Geological Survey, in cooperation with the authors, has placed a number of test panels. Among these test panels many grades of iron and steel, made by different processes and containing different percentages of impurities, are represented. Some of the plates are galvanized, some are tinned, and some are left in their original condition as received from the mill, with the ordinary coating of mill-scale. Inhibitive paint formulas have been placed upon a few of the plates, to determine whether a paint coating would be as serviceable as the tinned or galvanized plates unpainted. The writers do not feel that they have the delegated authority to analyze the results which are being obtained in this

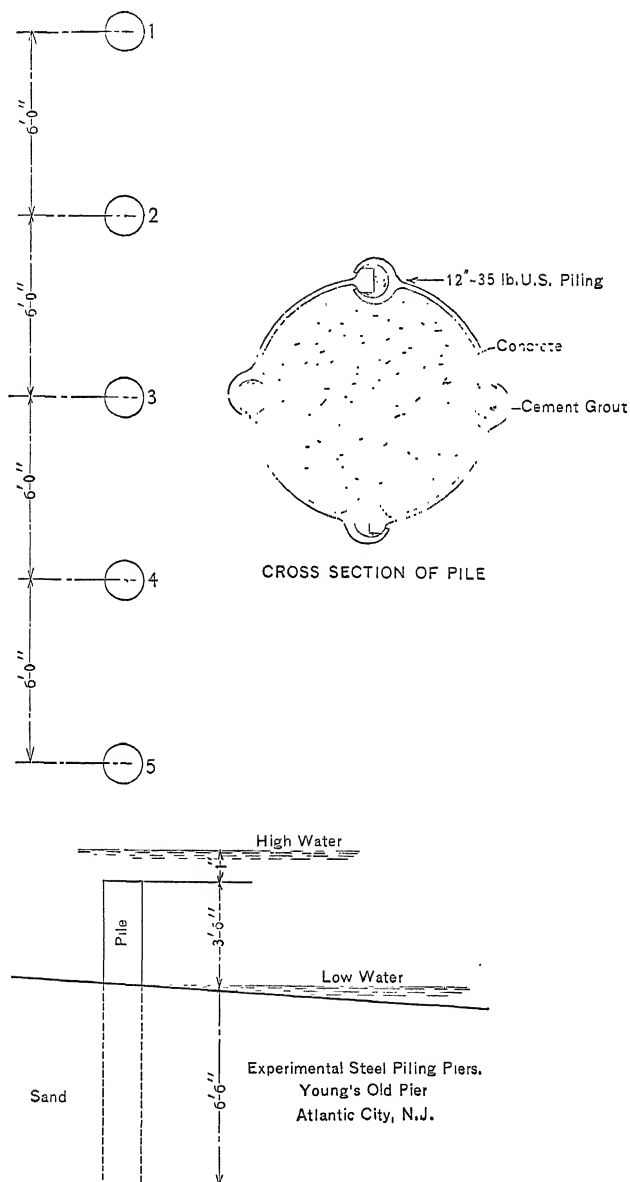


FIG. 63. — Details of Construction of Test Piling at Atlantic City, N. J.

series of tests, or to draw conclusions from them. They have been briefly described here to make the record of contemporary tests

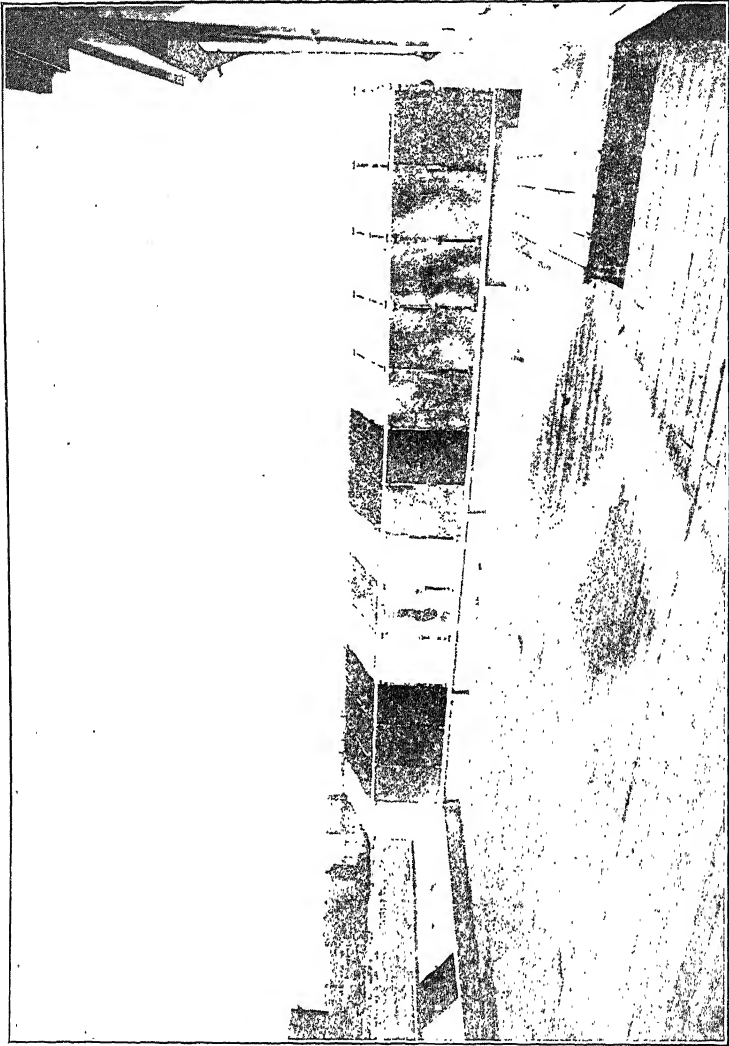


FIG. 64. — Test of galvanized and black iron roofing and sheathing, U. S. Geological Survey, Young's Old Pier, Atlantic City, N. J.

complete. The general appearance of these interesting tests is shown in Figs. 64 and 65.

Many other tests have been made at Atlantic City, upon the girders under the board walk, the steel piling under some of

the piers, and upon a series of plates exposed near the piers, and within a few years an abundance of useful information will be

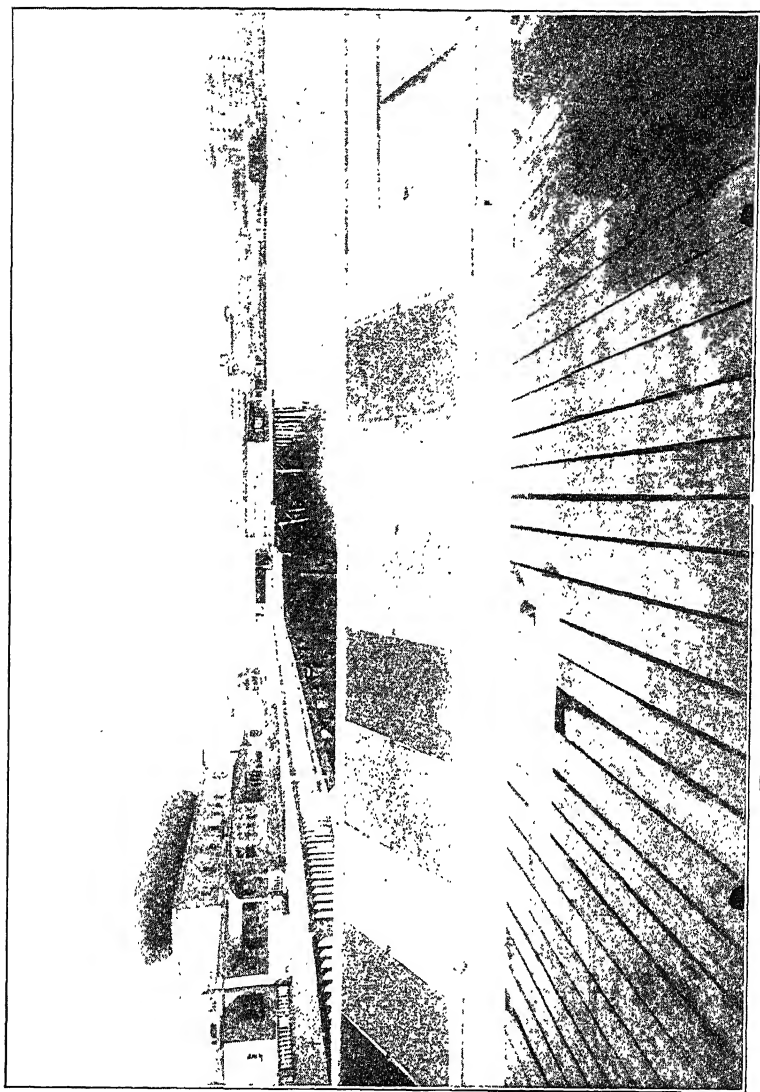


FIG. 65. — Corrosion effect on tinned plate.

obtained on the subject of protective coatings adapted for use in the neighborhood of salt water.

CHAPTER IX

PAINTS FOR VARIOUS PURPOSES

The Importance of the Special Design of Paint Formulae. — One single variety of paint can no more fulfil all the purposes for which protective paints are used than can one kind of paint serve all the demands for the proper decoration and preservation of wood. The controversy in regard to mixed pigments as against straight white lead house paints is analogous to that which contrasts the mixed pigment with the straight red lead prime coatings for structural metal. In a like manner the gum varnishes used on the interior woodwork of houses correspond in a sense to the lacquers so largely used on brass and other metals for which protection is demanded. It may be said that there is a paint for every purpose, in the same sense that there is a specialist in every field of scientific research and in every profession.

Throughout this book and in the tests that have been outlined, we have been mainly considering those pigments which, mixed in definite proportions, will afford the best protection in a general way for bridges, structural framework for buildings, and all work on a large scale. We have now to consider the painting of special forms of metal which, because of certain peculiar conditions which have to be met, present a special problem.

Galvanized Iron and Modern Methods Used in its Decoration and Preservation. — The painting of galvanized metal has always been considered by the master painter one of the difficult problems that must be met. Very large quantities of galvanized iron are used for siding and roofing purposes, especially in buildings and factories designed to be fire-proof. Railings, cornice work, gutters, drain pipes, fences and other accessories to the construction of buildings and the maintenance of property, are galvanized and put into service without paint protection. Efficient protection is not as a rule provided by the galvanizing processes, if the object is to preserve the metal for long periods of time, and paint-

ing must be resorted to in order to erect another barrier against the attacking forces which produce rapid corrosion and decay. The peculiar greasy nature of a zinc-coated metal prevents the proper adhesion of ordinary paints, so that peeling and blistering result. In order to secure the proper adhesion of paint to galvanized iron, several different methods of treatment of the metal have been suggested. Acetic acid in the form of common vinegar, acid salts, ammonia, sal soda, mixtures of copper salts with muriatic acid and sal ammoniac, are in more or less general use among painters, the object, of course, being to produce a slightly roughened surface to which the paint will adhere.

That these preliminary treatments are wrong in principle and quite unnecessary in practice, when proper paints are selected, is the firm conviction of the authors. The metals should, as a matter of fact, be given a priming coat of a sharp-toothed silicious pigment, ground in varnish. This should be well brushed onto the metal, so that the sharp angles of the pigment will form a union with the zinc surface. In short, the varnish serves the purpose of closely cementing the pigment to the zinc. In addition to the sharp pigment, a certain proportion of a soft pigment, such as sublimed or corroded lead, is believed by some experts to be beneficial. Subsequent coats of paint of any desired formula may be applied provided the first or priming coat is properly designed. Varnish vehicles have been tried in connection with soft pigments, such as carbon black and lampblack, with some success, as far as proper adhesion is concerned, but in the opinion of the authors silicious pigments properly mixed with some form of lead pigment are much better and safer to use.

Painting of Tinned Surfaces.—In the course of exposure tests near the seashore, which have been under the observation of the authors, in which the test pieces were tinned with five to forty pound coatings, the great importance of affording efficient paint protection of tinned surfaces immediately after erection was clearly shown. Some of the test plates actually showed evidences of rust at the end of two days' exposure, and at the end of a month nearly all were corroding rapidly. Tinned surfaces do not present as great painting difficulties as galvanized surfaces, and any good inhibitive composition may be selected for their protection. It is interesting to note that the use of graphite has been condemned by the Master Sheet Metal Workers' Associa-

tion as positively dangerous for application to tin roofs.¹ As evidence accumulates, it becomes more and more apparent that this pigment is a natural stimulator, and when used as a contact coat has been a contributing cause to the failure of many tin roofs. The authors have designed an inhibitive formula based on knowledge gained from research and practical experiments which has given satisfaction in this class of work. This formula is composed of 98 per cent. pure iron oxide with 2 per cent. zinc chromate, ground in properly aged linseed oil, with or without a certain percentage of varnish. The use of inert natural iron oxides or ground hematites for this purpose is recommended. It should be stated, however, that before painting, the tin should be wiped so that the palm oil used in the process of manufacturing tin plate will be removed from the surface. The use of turpentine or benzine is recommended for this purpose.

Bituminous Coatings and their Application for the Protection of Iron. — From the standpoint of the electrolytic theory of corrosion, it has repeatedly been stated in the foregoing pages that a natural insulator or non-conductor of electricity should be well adapted for the protection of iron. In view of the truth of this general principle it would seem that bituminous compounds were peculiarly well adapted for the purpose. Unfortunately, many materials which are well adapted for the protection of iron from one point of view are too prone to fail from another. As a matter of fact, most bitumens will not stand free exposure to atmospheric conditions, water, and sunlight. It is a significant fact that in the cases in which bitumens have been successfully used it has been under conditions in which the material was not, so to speak, normally exposed to sunlight and the atmosphere. Asphalts (and by this term is meant the natural bitumens found in nature) do not withstand the action of water without undergoing change. On the other hand, artificial bituminous substances such as coal tar, both crude and refined, although they are sufficiently waterproof, undergo certain changes under the action of sunlight and the atmosphere, which materially change their nature.² It is for just these reasons that bituminous coatings instead of coming into general use as protective agents have

¹ Proc. Second Annual Convention, Nat. Assn. Master Sheet Metal Workers Indianapolis, August, 1906.

² See illustration, p. 214.

found only a limited and special field of application. A careful study of the subject serves to show that the useful application of bituminous paints and dips is confined to the cases in which the action of sunlight is excluded. Thus we find the use of bitumen confined principally to the painting of pipe lines, smoke stacks, tunnel work, and piping generally. In short, to all cases in which either sunlight is excluded as a factor or where the temperature of the structure to be protected is so high that no other form of protective coating will serve. It is not the intention of the authors, however, to contend that properly refined coal tar, asphalts, and bituminous mixtures of various composition have not been used with more or less success.

The value of such compounds has been increased by admixture with fossil gums, among which kauri gum may be mentioned. By mixing lime with hot coal tar a valuable mixture has also been produced for pipe dipping and other purposes, and in the authors' opinion such a mixture as this is well adapted for many purposes. The possible development of the use of steel for railroad ties will demand efficient protection, for which, owing to economical reasons, the bitumens must be made available. This phase of the subject will be discussed in a later paragraph.

Baked japan coatings have come into general use in recent years. These coatings are compounded largely of high-grade asphaltic gums such as gilsonite and elaterite, sometimes mixed with a certain percentage of kauri or other fossil gums. The material to be coated is generally heated and then dipped in the hot mixture. In some cases the material is baked in ovens until the coatings become hard.

The well-known Angus Smith method of baking pipes coated with linseed oil, and afterwards immersing in tanks of heated coal-tar pitch, or coal-tar pitch admixed with linseed oil, was the original process which has been followed by many others, notably the Sabin process. Asphaltum or gilsonite mixed with linseed oil or mineral oil has also come into some use for this purpose and with considerable success. For information in regard to the technology of these processes, the original authorities should be consulted.¹

Regarding the Use of Coal Tar.—With regard to the use of

¹ See Sabin — *Technology of Paint and Varnish*. First Edition, 1906. John Wiley & Sons, New York.

coal tar, Wood,¹ a well-known authority, says: "A coal-gas tar paint that has given very good results in the coating of gas-holder tanks and other situations where the metal is exposed to ammonia and sulphurous acids in solution, and to alternate melting and drying under a great range of temperature, is made as follows: Coal-gas tar is well boiled to evaporate the water and light hydrocarbon elements, and then 20 to 25 per cent. of caustic quicklime is sifted and well stirred in to neutralize the acid elements in the tar. This is to be kept hot for a few hours and then an equal quantity of good Portland or hydraulic cement is sifted and stirred in thoroughly. The mixture is applied hot to the clean dry iron, and can be repeated soon as cool or dry if the exposure conditions are to be very severe. In the latter case, a little more cement should be added, so that the caustic lime and cement mixture will contain 50 per cent. of each. The pigments thicken the coal tar and prevent it from running under sun temperatures and give a bond to the brush coating of neat Portland cement that should be applied to the coal-tar coat as soon as either the first or second coat of the mixture is dry. This coating can be repeatedly applied with advantage. It is impervious to gases and water and has no tendency to run at temperatures under 130° to 140° F."

The views of Spennrath² are also worthy of citation in regard to the use of bitumens as protective agents: "Tar paints were at one time largely used for the prevention of rust, but their employment has of late fallen into disrepute, the alleged protective action having been shown to be of very doubtful efficacy. It is true that a coating of tar is altogether insusceptible to the chemical influence of the atmosphere and also to acids and alkalis; but, at the same time, the tar itself contains substances capable of causing iron to rust. Crude tar, for instance, always contains moisture, and, in addition to this, acetic acid is present in wood tar, the water and acid quickly causing the iron to rust. Hence it is that sometimes very extensive rusting can be detected, often to a considerable degree, under the tarry coating. Water-free or acid-free tar would not exert such action; but the purification of the tar from these admixtures is troublesome,

¹ M. P. Wood. *Rustless Coatings; Corrosion and Electrolysis of Iron and Steel*. First Edition, 1905. John Wiley & Sons, New York.

² *Iron Corrosion*. L. E. Andes. Scott, Greenwood & Son, London, 1900.

and increases the cost of this preparation, so that the advantages, as compared with oil paint, disappear. Finally, tar paints become softened by the sun's rays to such an extent that the mass runs and leaves the iron bare. Thus no security against rusting can ever be obtained by the use of tar paints."

An immense amount of work has been done in recent years on the chemistry of the bitumens, and more reliable information is now available in regard to their refinement and treatment than ever before. As a matter of fact, engineers have been inclined to speak of tar and asphalt as though these materials were standard substances in the same sense, for instance, as sugar and common salt are known as standard substances. We now know, however, that this is very far from being the case. The character and quality of these substances, as a matter of fact, varies within wide limits and is dependent not only upon their source but upon the methods of preparation and refinement. As an instance of this, it is only necessary to refer to the widely differing quantity of free carbon or soot carried by different samples of refined coal tar. It is not only possible, but highly probable, that a coal tar containing, say, less than 20 per cent. of free carbon would be better adapted for a protective coating than one carrying from 40 to 50 per cent. of this constituent. The following paragraph is included for the information of readers who may be especially interested in this phase of the subject.

*Tar Paints.*¹—Coal tar, if properly refined, makes an excellent paint or varnish, especially for metal surfaces which are subjected to the action of corroding gases. Crude coal tars vary greatly in composition, but always contain ammoniacal water which makes them unsuitable for use as paints. The presence of water greatly reduces the adhesive qualities of the tar, and ammonium salts tend to saponify some of the oily constituents, thus making them more or less soluble in water. A coating of crude tar is likely to blister and peel off in places shortly after application. Tars which have been boiled to remove the ammoniacal water are somewhat better than crude products, but are never as satisfactory as properly refined tar paints.

Besides ammoniacal water, coal tars contain at least two other objectionable constituents from the standpoint of paint manu-

¹ In the preparation of this paragraph the authors are indebted for assistance to Prevost Hubbard, who has made a specialty of the study of bitumens.

facture. These are naphthalene and free carbon. Both are the products of high temperatures to which the coal gases are subjected during the process of tar formation, and as they are usually present to a less extent on low temperature than in the high temperature tars, the former are to be preferred in the preparation of paints. Naphthalene is a crystallizable solid which is held in solution by the tar oils. It volatilizes slowly at moderate temperatures, although it is found mainly in the higher boiling fractions. If present in large amount, it makes a pasty paint which after drying commences to crack and disintegrate as the naphthalene volatilizes. Excessive quantities of free carbon produce a lumpy, uneven paint, which is deficient in waterproofing properties. Free carbon also gives the bitumens a false consistency. If present in moderate amounts, it is perhaps not an altogether undesirable constituent, as it adds to the body of the tar and serves to some extent as a filler. Twenty per cent. free carbon would seem to be the maximum allowable limit.

When refining a tar for the production of paint, it may merely be distilled until sufficient volatiles have been driven off to give it the desired consistency, or distillation may be carried to the formation of a moderately hard pitch which is afterwards cut back with certain of the distillates. The latter type is usually to be preferred. In the European countries, it is customary to employ an upright form of still with convex bottom for tar refining, but in the United States large horizontal cylindrical stills are commonly used. The process of distillation may be briefly described as follows: The still is first charged with crude tar, all openings except that leading to the condenser closed, and firing commenced. As the tar becomes heated it begins to froth and foam and if not carefully fired will boil over into the condenser. This is due to the presence of water which is converted to steam while the tar is still viscous. Boiling over may also be caused by an excessive amount of free carbon which causes the vesicles of gas and vapor to adhere to the carbon particles and thus swell the volume of tar. The removal of water in the final stages gives rise to a peculiar noise made by the steam, which is sometimes called the rattles. After this noise ceases, distillation usually proceeds without further trouble, and the distillate is caught in fractions according to the needs of the distiller. Thus, the following fractions may be collected:

- (1) First runnings to 110° C.
- (2) Light oils, 110°–170° C.
- (3) Carbohc or middle oils, 170°–240° C.
- (4) Heavy, dead, or creosote oils, 240°–270° C.
- (5) Anthracene oils above 270° C.

In the United States the distillate is usually divided into only two fractions, the light oils having a gravity of less than 1.00 and the creosote oils having a gravity greater than 1.00. The second fraction is collected until the residual pitch is of the desired consistency. If this pitch is sufficiently fluid it may be employed cold as a paint. It is preferable, however, to carry the distillation further and afterwards cut back the harder pitch with dead oils from which the naphthalene has been removed. Pitches which contain only the higher boiling oils as solvents for the heavier bitumens take a long time to dry, and for this reason it is sometimes preferable to use a harder pitch which requires to be heated before application, but afterwards dries rapidly. A still more satisfactory paint is one produced by cutting a moderately hard pitch with about three-fifths its volume of light oils. Such paints may be applied cold and dry in a comparatively short time. Rapid drying paints and varnishes may be prepared by substituting the more volatile tar naphtha for the light oils. They may be applied in very thin coats if desired by using a large amount of naphtha. Water-gas tar pitch makes an excellent base for these varnishes, as it contains but very small amounts of free carbon and naphthalene and produces a glossy black coating of uniform texture.

To sum up the discussion of the use of bituminous paints and compounds as protective coats for iron, the authors wish to reiterate their opinion that in special cases, and if properly selected, there are no better materials available. For use, however, under general exposure conditions where sunlight and free atmosphere are elements in the problem, bitumens cannot be successfully used. The well-known effect which has been mentioned in previous paragraphs as "alligatoring" is almost always produced on bituminous coatings exposed to the action of sunlight. This effect, which has been photographed from one of the panels on the Altantic City tests, is shown in Fig. 66.

An accurate explanation of the phenomenon spoken of as alligatoring is not easy to give, but it probably depends on a

superficial hardening of the outer or skin surface of the coating, underneath which the body of the material still remains to some extent plastic and elastic. The regular and diurnal expansion and contraction of the iron, which have sometimes been referred

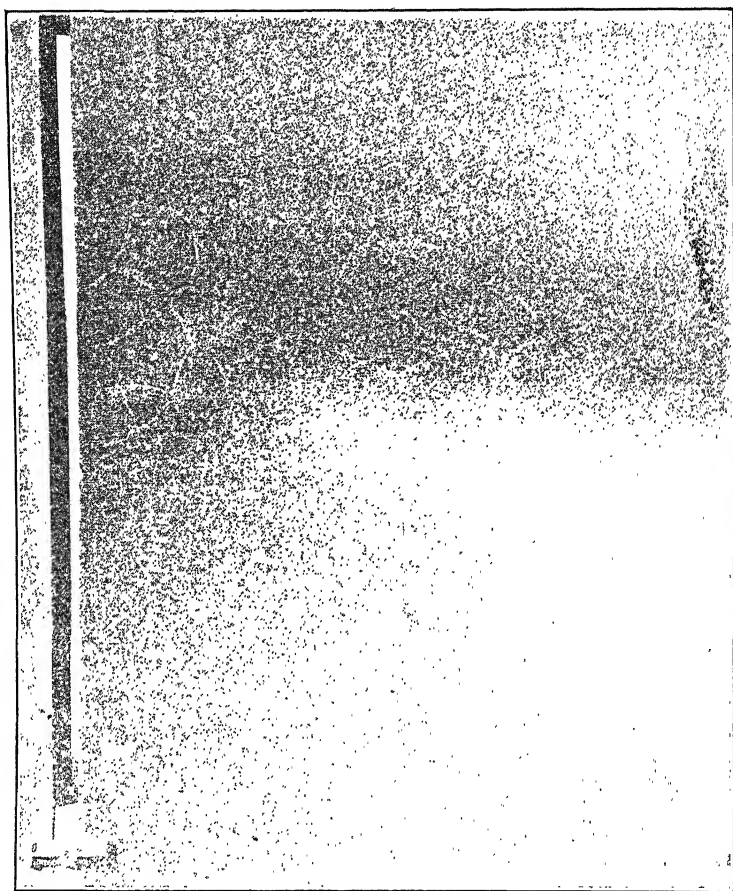


FIG. 66. — Alligatoring of coal tar over red lead.

to as the breathing of steel, must gradually produce this tendency to cracking or checking of the superficial layer of the bituminous coating. The effects produced are exactly similar to the crazing of vitreous glazes which has produced so much discussion in the ceramic industry. Exactly the same effects are produced in some

cases of linseed oil films in which an excess of unctuous or soft pigment has been used. It follows that if this checking effect spoken of as alligatoring continues for any length of time, the underlying surface will become exposed to the corrosion influences.

Paper Paints and Paper Preservatives. — A process proposed by Cross and Bevan has been described by Andés,¹ by which cellulose paper is dissolved in caustic soda lye, producing a highly protective paint. Paraffined paper has also been used successfully as a protecting material. For further information in regard to these rather unusual methods the reader is referred to the literature as given in Appendix B.

Painting Metals Subject to Marine Growths. — The dockage of steel ships which have been in the salt water for six months or more generally discloses a condition of surface below the water line that has caused naval constructors much concern. The thick crust of barnacles and marine growths must be scraped off if the ship is to make speed with the least coal consumption, but the tenacity that is shown in the adherence of the marine growth makes it impossible to avoid abrasion of paint coatings, in the cleaning process. That such growths are stimulators of corrosion there seems to be no doubt, and the only remedy seems to be in the application to the steel hull of the boat of a good, hard undercoat, with a top coat of paint containing materials which will act as poisons to the various growths, and prevent their action. Certain semi-drying compositions, containing pine tar or crude oil, and having a percentage of some powerful poison, such as strychnine, have been used as a vehicle for high-grade oxide of iron and lead pigments, and seem to have shown excellent results.

Soaps of copper, arsenic, and other poisonous compounds, made by precipitating a saponified oil with salts of the above metals, are often dissolved in the vehicle of marine paints and are undoubtedly of value, especially the soaps of copper. Corrosive sublimate and oxide of mercury (mercury vermilion) are probably the most efficacious poisons to use for this purpose.

The first, or under coating, for the ship plates should contain in the vehicle a good hard drying varnish to act as an excluder of water, and the outer coats should be those containing the poisonous pigments. A certain percentage of oil of a semi-drying nature is sometimes advisable.

¹ Der Eisenrost, p. 252.

Paints resistant to the action of sea water and saline atmospheres have already been discussed in a previous chapter.

Painting Steel Cars.—The equipment of modern railroads has brought about great changes during the last few years in the construction of both freight and passenger cars. The old type of wooden cars are rapidly being replaced by those of all steel construction, which are found to be safer and more efficient from every point of view.

Before painting steel cars, the surface should be, and usually is, cleaned with the sand blast. The sand blast has been found more efficient than paint removers for removing old paint from steel surfaces. Old paint, under the abrasive action of the sand from the blast, readily wears down, and the continuous action of the sand upon the steel furnishes a good surface for the application of new paint. In order to give proper smoothness, the surface may be coated with a primer which generally consists of a silicious pigment, such as mineral black, with the possible addition of some willow charcoal ground in oil and varnish to a thick paste. After this has thoroughly dried, a coat of filler is usually applied, and then a coat of surfacer, these materials being preferably of inhibitive pigments and of different colors so that the inspector may know by the color the number of coats that have been applied. Two color coats are generally applied upon the surfacer and then several coats of the finishing varnish may be used. The authors do not wish to convey the impression that the above general outline of car painting is recognized as standard, but it is their desire rather to indicate that in the various primers and fillers that are used for car painting, the replacement of stimulative pigments with inhibitive pigments should be made, and when this condition prevails, not only on the first and second coats but throughout on all coats, the best results will probably be obtained.

The ordinary type of sheet-steel coal carrier sometimes receives sand blast treatment and then spraying with paint, the small amount of time allotted the painter in his work requiring the use of excessive drier in order to get the cars second-coated, ready for lettering and stenciling, and out of the way to make room for others. Such methods should be revised. The authors have yet to see a car painted in the above manner that is not badly corroded in all too brief a period, and it is doubtful whether

many steel coal cars even survive their maiden trips without showing rust tuberculation.

The use of pneumatic paint atomizing machines by large railroads has reduced materially the labor cost per car, and has probably resulted in a more uniform distribution of the paint, especially on rough and irregular surfaces. The use of excessive quantities of thinners should, however, be avoided when paint machines are used.

The authors are aware of the numerous practical difficulties that the car painter and railroad engineer has to contend with. The modern steel coal-carrying freight car provided with lower dumps furnishes a specific instance of just such a difficulty. Our winter climatic conditions frequently cause the coal to freeze in the cars, so that in order to free the dump hoppers the railroad operatives find it necessary to beat upon the side of the cars with the nearest available weapon. It is evident that no paint coating that has ever been designed will stand such heroic treatment. The only practical solution of this difficulty which presents itself is some system of inspection and maintenance which will provide for repainting at frequent intervals in the yards without waiting until complete failure demands the return of the car to the shops. The old wise saw that a "stitch in time saves nine" finds a peculiarly appropriate application not only to the conservation of steel shaped into cars and other containers, but also to the subject of the conservation of iron in general. As a matter of fact, such a system of maintenance as is outlined above has to some extent been tried, and it is not altogether an unusual sight in freight yards to see corrosion spots on cars being touched up with red lead. As far as this work has been carried on it constitutes in the opinion of the authors one step in the right direction. There is no reason, however, why an inhibitive paint compound should not be designed and compounded to a definite color scheme, so that retouching under this plan of maintenance could be carried on by expert painters in the freight yards. Surely the cost of maintenance as carried out by such a scheme would not in the end be greater than the steadily fixed charges laid upon all owners and operators of structural steel by the never ceasing attack of corrosive influences.

Paints for Locomotives and Tenders. — In painting locomotives and tenders, large quantities of mineral black (a special grade of

bituminous slate), ground in varnish, is generally used for the primer. After rubbing down, this coat is often followed with one containing white lead, carbon black, and silica. This coating is followed, after rubbing, with a body coating of ivory black in japan, and finally with several coats of special locomotive finishing varnish. The use of mineral black is not bad practice, as it has no special stimulative properties. In the opinion of the authors, however, 2 to 5 per cent. of special inhibitive pigment should be used in admixture with the pigment.

Protection of Iron in Tunnel Work.—The protection of iron in tunnel work presents a problem of unusual difficulty. Constant seepage causes drippings of an extremely corrosive nature to come in contact with all exposed surfaces. Very often this exuded moisture found in tunnels is rich in chloride and other corrosive electrolytes. These salts act to a certain extent the part of paint removers. The atmosphere in tunnels is often rich in carbonic acid, sulphur dioxide, and invariably high in moisture content. These conditions call for the very best excluding and inhibitive paints that it is possible to design. It has already been stated that properly refined coal tar, treated with lime, is well adapted under certain conditions for use in the dark, and therefore should be useful in protecting the various forms of iron and steel used in tunnels. If oil paints are to be used, they should have a varnish vehicle of the highest type, made with gums of low saponification value, such as copal. A varnish paint of this nature has been found to give extremely good results on the cars running in the tunnels of the Pennsylvania Railroad under the Hudson River in New York City.

Painting Train Sheds.—The train shed with its gigantic network of structural metal is constantly filled with the sulphur-laden gas belching from the numberless engines that operate therein. This gas condenses with the rising steam upon the painted metal surface, and often causes most disastrous results. In the large terminals a force of men are kept constantly at work repainting the maze of steel. The engineer is ever on the lookout for some material that will last for a greater length of time. Excluding the fumes and gases by the use of a varnish paint seems to offer the best solution of the above problem. The varnish for such a paint must be, however, of the highest grade, and one that will withstand exposure without cracking or checking.

The use of high-grade copal gums for this purpose is to be recommended.

Black japan made by fusing and properly treating eight pounds of kauri or copal gum in two gallons of oil, and mixed with about twenty gallons of boiled linseed oil containing 1 per cent. of litharge, forms a base into which may be added five gallons of high-grade asphaltum. When this composition is applied, it dries to a high glossy surface and forms an excellent excluder. Other paints, made of inhibitive pigments and possessing excluding vehicles, have also proven most satisfactory for the above class of work.

Paint Protection for Water Tanks. — Water tanks and other large steel containers present a double problem, as protection must be provided on both the inner and outer surface. The painting of the inside of steel water tanks has been in practice on American railroads for some time past. F. C. Peterson¹ of the Southern Pacific Railroad has recorded satisfactory results with the use of a formula composed of 25 lbs. dry red lead, 5 lbs. litharge, 5 lbs. Venetian red, 1 gallon boiled linseed oil, and 1 gallon of turpentine. Three coats are usually given with this mixture. The use of natural hematite (iron oxide) in place of the Venetian red would be better practice. Venetian red generally contains fifty per cent. or more of gypsum, which is partially soluble in water and is often the cause of the rapid failure of paint films. The results obtained with gypsum on the Atlantic City test panels would certainly not recommend its use in an inhibitive formula.

Painting Steel Railroad Ties. — The rapid diminution of our forests, and the increasing cost of wood, may ultimately require the substitution of steel for railway ties. Steel ties are at present being experimented with on several railroads, and, while they have not as yet proved wholly satisfactory, some progress has been made, and we may feel certain that their final adoption in some form is sure to come. Steel ties must be protected or corrosion will soon weaken and destroy them, reducing their durability below that of the wooden tie. If, however, they are properly protected, there is no reason why they should not last for many

¹ Painting Insides of Steel Water Tanks. Paper read before the Maintenance of Way Master Painters' Association, Niagara Falls meeting, September, 1909.

years. The authors believe that dipping in hot properly refined coal tar free from acid is the best treatment that has been suggested for the purpose. A mixture of 80 parts of coal tar, 5 parts of dry lime, and 15 parts of Portland cement is recommended as a good formula for a tie dip. The lime which in itself is an inhibitor neutralizes any free acid in the coal tar, while the cement appears to lead to a harder surface, which gives more resistance to the abrasive action of roadbed dust. In addition to this, it might be advisable to apply a preliminary dip coating designed to be inhibitive. The first cost of these treatments will be high, but if steel is to be used for the purpose, some such protection must be supplied.

The operation of refrigerator cars would constitute a special menace to steel ties, unless mechanical devices are contrived to catch and discharge the brines. The Master Car Builders' Association has appointed a committee to study this problem. In a paper on this subject, A. B. Phelps¹ of the Lake Shore Railroad says: "To those of you who have the care of bridges, interlocking plants or other iron or steel apparatus or other structures, I need not enlarge on the destructiveness of salt brine; to those of you who are not on trunk lines, and consequently have few, if any, refrigerator or stock cars passing over your road, I will simply say that salt is one of the most destructive agencies to steel and iron of which I know, and when brought in contact with steel bridges, if neglected, soon forms large, thick scales of corroded metal, greatly weakening the structure, and requiring the use of heavy hammers or chisel-pointed steel tools to remove them. Ordinary steel brushes will have no effect whatever on them.

"This salt brine, of which I speak, is formed by the melting ice and salt used in cooling the contents of the car, and is allowed to drip directly from the bottom of the car, almost exactly on, or only a few inches from the rail, alighting on both the top and bottom flanges of the bridge, where it proceeds to get in its work of destruction. To prevent, not to cure, this evil is my theme. The present general construction of these cars is to provide an outlet underneath the icebox of about a 2-in. iron pipe, protruding into a metal cup, or box, holding about a quart, which,

¹ The Destruction of Railroad Property by Refrigerator Car Drippings, Sixth Annual Convention Maintenance of Way Master Painters' Association, 1909.

when filled, forms a trap, so that warm air will not enter the ice-box from beneath. This cup is allowed to fill and spill, and slop, and drip its contents the entire length of the road, and do its hellish work — that is strong language, but no stronger than the solution of which we are speaking. These conditions should never exist, and should not be allowed for one single day. Provision should be made, in building these cars, to retain the brine and carry it to and empty it at the terminals, or at the icing stations.”

Inhibitive Pigments for Railroad Equipment in General. — Red lead, basic lead chromate, zinc chromate, and bright neutral oxide of iron are inhibitive pigments which may be used in producing reds for semaphore, signal and switch targets on railroads. Genuine oxide of chromium is a most permanent green pigment, when this color is desired, for the above use. When this pigment is reinforced with a silicious pigment, its wearing value is increased without materially detracting from its color depth. Zinc-chrome green made from zinc chromate and inhibitive Prussian blue, is also a very permanent inhibitive color that should meet favor for signal work.

All these pigments have been experimented with and carefully observed by both the authors under a wide range of service conditions, and are known to have given satisfactory results.

The Preservation of Steel Mine Timbers. — The question of the substitution of wood by steel for timbering mines, is an important one from several points of view. An enormous amount of valuable timber which might possibly be employed to better purpose above ground is used in mining operations. On the other hand the fear of rapid and dangerous corrosion of steel induced by the acid character of most mine waters has led many engineers to feel that the substitution of steel for wood might lead to extensive failure in the course of time. Woodworth has made an extensive research on this subject,¹ in the progress of which he has reached the following conclusions:

“The application of economic principles to the use of steel demands that the life, on which its economical use is predicated, be lengthened to as long an extent as possible, and the prevention of waste and loss in the steel itself by preservative treatment.

¹ R. B. Woodworth, M. Am. Soc. C. E., Engineer Carnegie Steel Co. Paper read before the West Virginia Coal Mining Institute, Huntington, W. Va., December 7, 1909.

No iron has ever been or ever could be manufactured that would not rust in moist air unless it is protected by some sort of covering, for the reason that pure iron itself has a tremendous affinity for oxygen and the slightest contact between iron and oxygen in a more or less unstable condition causes immediately that combination of iron and oxygen which is known by the name of oxidation or rust. This tendency to corrode is characteristic of the metal itself and is independent of the presence of the impurities it may contain.¹ Iron does not rust when entirely submerged in pure water or water not containing free air; neither does it rust in a perfectly dry atmosphere, the beginning of oxidation being due to the presence of sufficient quantities of free oxygen, due to impurities contained in the air, in the presence of sufficient moisture to act as water of disassociation, this condition permitting the escape of hydrogen and the consequent oxidation of the steel or iron. The great variation which occurs in the rusting of iron and steel is probably due to unequal distribution of the impurities necessary in their manufacture. Iron does not occur in a pure state and in the process of the manufacture of wrought iron and steel, small traces of impurities occur more or less unequally distributed throughout the mass. It has been claimed that the small proportion of manganese which steel contains adds greatly to its oxidizing tendencies. This, however, is not borne out by actual experience and the removal of manganese does not carry with it freedom from oxidation.² The difficulty lies not in any one cause or element contained in the steel but in their unequal distribution throughout the steel which permits differences of potential at different points. The prevention of this oxidation, however, is a very simple matter. Such steel as has already been installed in the mines of the United States has given entire satisfaction without any serious corrosion and without any protective treatment other than the use of preservative paint. In wet mines in England steel girders are frequently tarred before being put in, but the actual loss from corrosion is so small as to be a minor quantity even when the steel is not painted. In dry locations there is not much danger of any serious corrosion. In the speaker's judgment, however, true economy will require the painting of all steel for underground operations with one shop coat of good

¹ The authors are not prepared to accept this unqualified statement as has been shown in preceding discussions.

² This statement may also require qualification.

paint and with at least one field coat. If these are well worked in, the steel should need no further attention for years. What these coats should be has been the subject of considerable investigation, attention being had as well to atmospheric conditions as to the possibility of contact with acid waters, and while laboratory experiments have not been finally completed, the broad lines of preservative treatment may now be indicated. Steel should not be painted with carbon paints in whose manufacture sulphuric acid has been used and the use of coal tar products is, therefore, to be avoided. The natural carbons, such as graphite, and hydrocarbons, such as asphalt and gilsonite, may be recommended for second coat work if properly ground and mixed with a good vehicle. For the first coat pigments should be used of a more or less inhibitive character, though it has been demonstrated that some of the best paints are not entirely inhibitive. The oxides of iron, such as Venetian reds, are usually manufactured by chemical processes and their use is to be avoided, though a good natural oxide of iron paint may be used under dry atmospheric conditions.

“The correct theory which underlies the prevention of corrosion in iron or steel is based on the use of a practically inhibitive pigment to prevent the inception of corrosion in the steel and the use of a second coat to protect the first from atmospheric and temperature conditions and to fill up thoroughly any vacancies or voids which may occur therein. To meet these conditions the pigment should be practically inert and its particles extremely small. While red lead is not absolutely inhibitive, it has been demonstrated in all kinds of exposures to be a first-class pigment for use in the preservative treatment of steel in almost any situation and its particles are extremely minute. It is a very heavy pigment and settles quickly, necessitating the mixing of a new lot if it has stood over any length of time. The settling may be retarded by the use of barytes or asbestine, and the use of the latter is to be recommended by reason of its permitting a firm hold on the pores of the steel. The oil should be pure, as the matter of vehicle is of large importance, and the raw oil is better than the boiled. A mixture of red lead, oil and asbestine, in the proportions of at least 15 pounds of red lead and 2 pounds of asbestine to a gallon of oil, with sufficient japan drier to work well, may be recommended as probably the best under present

conditions, and the use on this of a first-class graphite paint will serve thoroughly to protect the shop coat and to fill up any vacancies or voids therein, the particles of well-ground graphite being also extremely small. In the painting of steel the surface should be most carefully cleaned from all scale, rust, dirt, etc., and the paint should be applied in dry weather. No painting should be done in wet or freezing weather. When, for any reason, it is necessary to repaint, the repainting should be done on clean surfaces absolutely free from all rust, paint skins, dirt, etc. It is not sufficient to apply a new coat of paint over an old paint surface under which traces of corrosion appear; the new paint will cover the old surface and may adhere firmly thereto, but the corrosion goes on underneath just the same. This small attention to detail characterizes all thorough work and is necessary for the entire preservation of steel or iron in any location. It is doubly necessary by reason of the fact that underground steel may not be examined and repainted with the readiness possible in above ground construction. At the same time it may be added that underground conditions are not nearly so secure on the steel as above ground conditions, and certainly the paint itself is not exposed to those alternating conditions of high and low temperatures, dryness and wetness, strong light and darkness, with which above ground construction has to do and which are especially accelerative to the deterioration of protective coating. The only serious condition underground is due to the presence of acid-laden waters, and the speaker's chemical analyses and laboratory investigations indicate that the objections due to this cause have been largely overstated. Experience and theory all indicate that only the simplest means are necessary for the absolute guarantee of an extremely long life for steel used in underground conditions."

Painting of Steel Mine Timbers.—In a special communication to the authors Mr. Woodworth gives an account of extended laboratory researches on the subject of painting steel mine timbers: "Mine water usually carries with it more or less free acid and its corrosive action is one of the reasons advanced why steel should not be used in substitution for the standard wooden construction, and this in spite of the fact that an experience of fifteen years in the use of square timber sets has proven that material can be very well protected from this corrosive action by the use of methods recommended in ordinary outdoor structural work.

Conditions in mines vary greatly; in the long, dry passageways there is little danger of deleterious action; in damper situations there may be running water carried in the side ditches, which may come in contact with the feet of the timber sets; and at shafts the timber may be exposed to the constant action of running water which may be more or less acid in accordance with the character of the overlying strata which may or may not contain beds of coal. To find the best methods of protective treatment to meet the worst conditions, laboratory tests were instituted.

Samples of mine water were obtained from a number of anthracite and bituminous coal mines which were carefully analyzed in the laboratory of the Carnegie Steel Company at Homestead Steel Works for total solids and total free acid in parts per million, as shown on tables attached. From a comparison with a fuller analysis made by the Lehigh Valley Coal Company it was decided that practically the worst condition to be met would be that of an acid water containing 2320 parts of free sulphuric acid (H_2SO_4) in a million and 128 parts of ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$. To expedite the action of the acid water on the samples to be tested it was decided to intensify ten times and to subject samples to a solution containing 23,200 parts of sulphuric acid and 1280 parts of ferric sulphate to the million. In this connection it may be stated that investigations indicate the intensifying action of ferric sulphate in solution as compared with a solution containing sulphuric acid only. A mixture was prepared with 180 cubic centimeters of commercial sulphuric acid of 1.84 specific gravity and 79 drams of commercial ferric sulphate dissolved in one meter of water, giving 2.616 per cent. free sulphuric acid and .432 per cent. ferric sulphate, or 2.135 per cent. SO_3 and .432 per cent. FeSO_4 .

One-half in. round steel rods $3\frac{3}{4}$ in. long were used for test purposes, with wide mouthed bottles $4\frac{1}{2}$ in. high and $1\frac{7}{8}$ in. in diameter with necks $1\frac{3}{8}$ in. in diameter. The rods were painted with the pigments to be tested, inserted in holes bored in the corks and immersed in the above-mentioned solution, the bottles being properly labeled with the number of the pigment tested and the rods being marked by a file with the same number. Examinations were made at intervals of two or three days apart in the inception of the test and at longer intervals on such pigments as remained. The rods which showed a deterioration of pigments under solution action or corrosion underneath the films

were removed when such deleterious action became pronounced. Solutions were renewed when the reddish discoloration produced by solution action became pronounced provided the pigment showed no apparent signs of disintegration. The bottles were freely agitated at all such examinations and repeatedly between examinations as well. In some instances the solution continued clear and the pigment intact until the completion of the tests, which extended from December 23, 1908, to June 4, 1909, at which time the relative values of the pigments had been demonstrated.

The pigments tested were in part commercially prepared ready mixed paints, in part paints prepared from the raw materials in the laboratory, and in part special formulas furnished ready mixed by the Paint Manufacturers' Association of the United States. The vehicle used in the preparation of pigments in the laboratory was selected raw linseed oil purchased from the Pittsburg Plate Glass Company. The material painted was carefully cleaned from all mill rust, scale, etc., and the pigments applied carefully by brush. The first coat was allowed to harden thoroughly, some seven or eight days, or longer if necessary, before the application of the second coat, and the second coat was firm and hard in all cases before immersion in solution.

In one or two cases the pigments failed utterly in two or three days from the inception of tests. In others the action of the acid water produced almost immediately a marked discoloration without further change or deleterious action for long periods and without any precipitation of solid matter. One hundred and thirteen different combinations were tested and after expiration of the tests thirty-one remained. The purely carbon paints, presumably manufactured from coal tar products, gave no good results; natural oxide of iron showed up fairly well. The best pigments, both for adhesion and for minimum deterioration of film and minimum corrosion underneath the film, were red lead and the graphites.

On the basis of the results obtained in the execution of these tests it is recommended that steel mine timbers be painted at the shops with one coat of red lead and oil, mixed in the proportion of at least 15 pounds of red lead and 2 pounds of asbestine to a gallon of pure raw linseed oil, with sufficient japan drier to work well under the brush, and that a field coat be applied of first-class

graphite paint. Material to be thoroughly clean from rust and mill scale before painting. The theory which underlies this recommendation is based on the use of a practically inert pigment, thoroughly tried in all sorts of conditions, of firm adherence to metallic surfaces and of extremely small particles; and also on the use of a first-class excluder of likewise fine particles and firm adhesion thoroughly to protect the shop coat and to fill up any vacancies or voids therein."

The tabulated results of Woodworth's laboratory experiments, which were courteously turned over to the authors for use at their discretion, were not included here owing to the fact that a large number of the paints experimented with are proprietary compounds. Woodworth's own summing up of his experiments has, however, shown that he came to the conclusion that a good grade of graphite on top of a good grade of red lead primer was best adapted to the purpose, and provided the most efficient protection among all the compounds and methods of painting tried. With this conclusion the authors find themselves in complete accord, under the conditions which maintain in the experiments. The attack of free acid here was very strong, and, as Woodworth points out, ten times stronger than is found in the average mine conditions. It is quite evident that under such conditions as these the primary object must be to select a pigment which will be highly resistant to acid attack. It is clear that of all pigments in common use no one is more resistant to the attack of mineral acids than carbon in its graphitic form. The conclusion of Woodworth, therefore, that a good reinforced inhibitive prime coating, topped with a good acid resisting excluder, is the best combination that could be used under the circumstances is in accordance with the opinion of the authors. The question, however, as to whether red lead is the best inhibitive primer which could be selected for the purpose has not yet been convincingly shown.

The Painting of Field Fence Wire. — Galvanized zinc coatings are almost exclusively depended upon for the protection of field fence wire. This subject has been discussed in detail in a previous chapter. There can be no doubt of the fact that it is possible to prolong the life of wire for many years if the trouble is taken to place upon the zinc surface a top coating of properly selected paint.

The painting of fence wire presents certain difficulties that are not met with in any other class of work. The round surface of the wire causes paint of the ordinary consistency to run from the upper part, where a thin film is left, to the under part of the wire, where it collects in quantity, forming thick, non-drying clots which absorb moisture. The authors have found that the best consistency for paint to be used on wire fences should be that possessed by a highly viscous cream; in fact, a thin paste is often advisable, if properly brushed out. A good soft hair, flat varnish brush about $\frac{1}{2}$ -in. wide has been found the best conveyor for the paint. After the paint has been applied to the top and side of a wire fence for a considerable distance, the painter should go back and run the brush along the bottom of the wire so that the paint that has collected there will be uniformly distributed. Turpentine or other volatile diluents should not be used, and if reduction is found necessary, it should be with linseed oil, either raw or boiled.

A quart of paint will cover something over 300 ft. of ordinary eleven-strand fabricated wire field fence. For the painting of the fencing surrounding a large farm, only a few gallons, therefore, would be required. It is not necessary to employ expert painters to apply paint to wire, and when ordinary care is exercised the farmer or his men can easily paint fencing at their leisure. The increase in the durability of the fence which painting provides should induce the farmer and other consumers to undertake the work even though it involves a certain amount of time and trouble.

A recent inspection of the Steel Wire Test Fences at Pittsburgh by the authors indicated very clearly that the wire panel which was painted with an inhibitive formula was outlasting all other panels on which ordinary paint coatings had been used. The use of finely ground hematite with a small percentage of zinc chromate, ground in pure linseed oil with or without the addition of varnish, should prove efficient for use on fence wire. Silicious primers, mixed with zinc or red lead, are also being used for a first coat on galvanized wire. Paints containing stimulative pigments, in the opinion of the authors, should not be employed on wire fencing, as they are almost certain to cause rusting and may even hasten the decay of the underlying zinc. Fig. 67 shows the effect produced on ungalvanized wire in less than one year when a stimulative pigment has been used.

Care should be taken to paint when the wire is perfectly dry. Moisture will lead to subsequent failure, causing non-adherence, blistering, and destruction of the film. Painting in very cold weather should also be avoided, as puckering and contraction of the paint skin will result.

In nurseries, vineyards, and certain other places, a spray of copper sulphate is sometimes used as a destroyer of the animalculæ that live upon the growing plants. When this copper

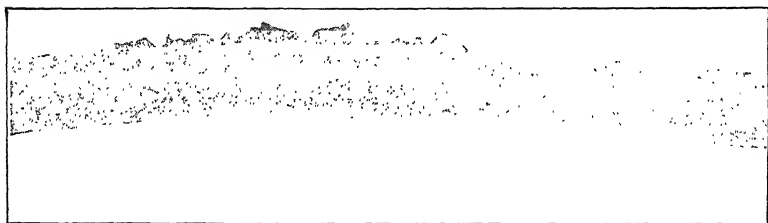


FIG. 67. — Section of wire painted with stimulative pigment. Enlarged. Failure resulted in less than twelve months.

sulphate strikes the zinc-coated wire upon which the plants are supported, the zinc at once goes into solution and the copper is precipitated in a loose spongy mass upon the wire. Moisture at once attacks the imperfectly protected iron and serious corrosion proceeds.

If the wire supports for plants are coated with a good protective paint, the above difficulties are to a large extent overcome, and chemical insecticides can be used without producing serious damage.

The authors have discussed with the manufacturers the possibility of shop coating galvanized wire fencing with inhibitive compounds, but the perfectly reasonable objection has been raised that wire so treated would not withstand the abrasion due to transportation, handling, and mounting on the fence. For this reason it would seem that the painting of fencing should be done in place and after they are mounted on the posts.

Prime Coatings for Structural Metal. — It is always difficult for the engineer to decide what paint formula should be used for the prime coating on structural framework for modern buildings. Probably red lead is in most general use for this work, where it has been found to give, generally speaking, a hard and

satisfactory base upon which to place the finishing coat. Andes¹ has stated in this connection: "We know that red lead forms a paint that strongly adheres to and hardens on iron, which it preserves from rusting; and we also know that the same paint is very durable when covered over by subsequent coatings of good paint. On the other hand, red lead paint, by itself, must, by reason of its small proportion of oil, soon perish under atmospheric influences, and is therefore unsuitable for use as a finishing paint. Now there is another point of great importance in connection with painting on iron, namely, the teaching of experience that although a paint rich in oil or varnish may be applied over a paint containing a high proportion of pigment to varnish, yet the converse practice must not be pursued; and this is the reason why the idea of painting with red lead was originally hit upon. This experience primarily applied only to wood, but it seems also to have held good for iron. The words 'it seems' are used advisedly, since no reliable experience to the contrary appears to have been gained, or at any rate published.

"In most cases, though not always, iron structures receive a first coat of iron or red lead oil paint in the works when completed, *i.e.*, when the individual girders, stays, etc., have been riveted and wrought into the most suitable condition for delivery. Nobody, however, troubles about whether the girders have been riveted out of doors—where they are exposed to the air and, more especially, to the deposition of moisture brought about by fluctuations of temperature—or under cover; and still less is any thought bestowed on the painting of the rivet holes, the stems of the rivets or the under side of the rivet heads. In many works the paint is laid on by day laborers who simply daub it on, often without suitable brushes, and the work is regarded as properly done if the metal is outwardly covered over with paint. Now the author readily admits that painting the rivet holes, and the rivets themselves, is a very tedious and often expensive task, and that very often there is insufficient space available for the rivets to dry after painting. Nevertheless, he holds that when it is a question of properly painting ironwork so as to fulfil the requirement that all parts of the metal shall be thoroughly covered, and that the connections, in particular, shall be so carefully painted as to prevent the incursion of water, then all these considerations

¹ L. E. Andes. *Iron Corrosion*. Scott, Greenwood & Son, London, 1900

of reducing the cost of production to a minimum must be put into the background."

Zinc chromate, high-grade oxide of iron, and other pigments have proven equally as efficient as prime coaters, as red lead. For further information on this subject, see Chapter VIII on the results which are being obtained on the Steel Test Panels at Atlantic City, which should be watched with interest by engineers.

As has been pointed out in a previous paragraph, red lead is not a standard substance and its inhibitive value may be easily affected by the process of manufacture by which it is prepared. As is described in a separate paragraph in a succeeding chapter, red lead is manufactured by two separate and widely different processes. It is not at all probable that the two products would show the same inhibitive value, as this value would depend upon the amount and character of the included impurities.

The Use of Oil as a Shop or Prime Coating. — The subject of shop coatings for machinery and structural iron has received a great deal of attention. It has long been known that linseed oil is an active stimulator of corrosion when applied to iron, when its surface becomes abraded in the least degree. This opinion is borne out by recent work done by Walker. Walker's work on this subject has been referred to in a previous paragraph, but in view of its direct bearing on the subject under discussion, it will be well to recapitulate it here. Walker finds linseed oil to be, under certain conditions, an accelerator of corrosion. When a steel or iron surface painted with linseed oil becomes abraded at a particular spot, corrosion proceeds more rapidly in the presence of the coating of oil than without the coating. This is ascribed to the fact that the hydrogen, which is always evolved when iron rusts, is constantly removed by the linseed oil, which (being an unsaturated hydrocarbon) has the power of absorbing hydrogen and therefore acts as a depolarizer much in the same way that mill-scale acts by destroying the so-called "electrolytic double layer."¹ When, however, linseed oil contains pigments there is a marked decrease in the power of the oil to remove the hydrogen and act as a depolarizer.

Perry² in commenting on the subject of shop coatings for

¹ See Chapters II and III.

² Bulletin No. 15, Scientific Section, Paint Manufacturers' Association of U. S.

metal, states: "The addition of high-grade fossil resins, carefully compounded with a carefully treated oil, adds greatly to the power of a paint to resist penetration by gases and moisture, producing a better excluding paint and at the same time adding to the appearance. The glossy surface which a paint made along these lines possesses, renders the paint a better repellent or resister of moisture. The quality and percentage of gum used influences to a great extent the wearing properties of this kind of paint.

"During the transportation of machinery and structural steel from the factory to the field and the workshop, there is met a state of condition that causes rapid corrosion. Moisture and gases attack the metal and assert their destructive action. In the past these results have been partially overcome by swabbing the metal with crude oil, in some cases, and, again, by giving the metal a dip in hot linseed or other drying oils or by applying tar and cheap paints as shop coats. The crude oil leaves upon the surface of the metal, even after wiping, a quantity of non-drying mineral oil which interferes with the drying of the paint coat which is afterward applied at the time of the assembling of the metal. It also prevents the paint coat from properly adhering to the steel surface, and this coat of crude non-drying oil, which still exists between the metal and the paint coat, is a source of never-ending trouble, causing peeling and shriveling. This crude oil treatment, therefore, should be avoided whenever it is intended that the steel is to be subsequently painted with oil paints.

"Where linseed oil instead of crude oil is used, a film of the oil is left upon the metal and rapidly oxidizes to a coat of linoxyn. This coat will protect the metal for a certain period of time, but is extremely porous and ultimately admits moisture. If, within this coating of linseed oil, there had been contained a proportion of pigment, or if the linseed oil had been developed by gums into a varnish or lacquer, then the excluding properties of the linseed oil would have been increased, and, if the formula were inhibitive in nature, the steel would be better protected from corrosion, and the application of future coats of paint, after assembling the steel, would have been practical and facilitated."

Mulder¹ states his views on the subject of shop coatings as

¹ Iron Corrosion. L. E. Andes. Scott, Greenwood & Son, London, 1900.

follows: "Since boiled linseed oil dries, on wood, to form a not very hard layer of varnish, it cannot be anything else but prejudicial to the adhesion of the subsequent paint, on iron, when the paint is separated from the metal solely by a layer of such linseed varnish, especially since the latter is, according to instructions, applied to the warm iron, a method which, in turn, cannot promote adhesion.

"This meaning will become clear if we imagine what would take place if the iron were coated with copal varnish. It is true that the residual varnish left by the drying of the linseed oil is tougher, and in so far better, than copal varnish; still it is a varnish all the same. Now it is essential that the iron should be coated with a very adhesive paint, which will afterwards dry hard and fast, and that all intermediate layers should be avoided and dispensed with; consequently the use of linseed oil as a first coating for iron is to be discouraged."

The authors desire to call attention to one point in connection with shop coatings, which has very generally been overlooked. The point referred to is the possible adhesion or absorption of water on the surface of steel. When kept in a humid atmosphere, at ordinary temperatures, the surface of steel is never quite dry, however much it may appear to be so. The consequence is that these layers of moisture are enclosed between the surface of steel and the protective coating. That this is a contributing cause to future trouble, if not failure, can hardly be denied. Mr. J. E. Stead, F. R. S.,¹ a member of the council of the Iron and Steel Institute of Great Britain, has stated: "That when ships' plates were made at steel works, identification marks were frequently made with paints while the plates were hot; and it was remarkable that ten or twelve years afterwards, when the ships' bottoms were cleaned they found the steel uncorroded where the marks had been made. That pointed directly to the best method of protecting steel and iron. They ought to heat the metal so as to remove every trace of moisture from the surfaces, and then apply the paint to the hot metal. There was always a little moisture, which adhered to the surface of cold steel plates, after they had once been moistened, even when they appeared dry, and probably that was responsible in some measure for starting the corrosion under the paint applied to cold surfaces."

¹ Journ. Iron and Steel Institute, I, 1909, p. 98.

Commenting on this important subject, Wood¹ states: "There are hundreds of records of the painting of important railway structures, where the first coat of boiled oil method was used, and, in the great majority of instances, the utter and rapid failure of the coating and the extra corrosion of the structure could be directly assigned to this so-called method of protection. The weather-resisting power of an oil coating is almost *nil* as compared with paint."

"A foundation coat of oil is a direct cause of the blistering and peeling of the coatings spread over it. It is seldom dried enough before the other paints are spread over it to ensure a close adherence to the metal it covers. When the subsequent coats of paint are spread, the solvents and oils in them soften to some extent the underlying coat of oil, and a moderate heat from the sun causes the whole coating to blister or peel. Too much oil in a paint coating, particularly if the surplus oil is in or near the foundation coat, whether on a wooden or metallic surface, will generally cause peeling, regardless of the pigment used in the coatings."

That linseed oil when used without pigments is not a desirable material for the prime coating of metal seems to be the universal opinion of authorities on the subject of the protection of iron. Further comment on the subject may be of interest. Brown² says: "The most insidious enemy of the iron bridge is rust, and the primary object of painting it is to protect it from those elements which cause destruction by rust. Rust is caused by the combination of the metal with oxygen to form the hydrate oxide of iron. This oxygen may be obtained from the air, from water, or from some other substance which acts as a carrier of oxygen or an oxidizing agent — always, however, in the presence of moisture. Now, one of the primary things to be considered in choosing a paint for ironwork is that it shall not contain in its pigment or vehicle any substance which is chemically active in such way as to convey oxygen to the iron. For if such a chemically active agent be introduced into the paint, sooner or later it will

¹ M. P. Wood. *Rustless Coatings*. First edition, John Wiley & Sons, New York, 1905.

² Edward Hurst Brown. Conditions that Must Be Met in the Ideal Paint for Railway Bridges. Proc. Third Annual Convention Maintenance of Way Master Painters' Assn. of U. S. & Canada, New York, Nov. 13 and 14, 1906.

promote rather than prevent rust. Of course, so long as the oil, in an oil plant, remains intact, it envelops the particles of pigment and keeps them away from the iron, but in time the oil, which has hardened by absorbing oxygen from the air, begins to disintegrate by the action of water coming from rain, hail, snow, or fog. Moreover, even the freshly applied oil is not absolutely impenetrable to moisture, as has been shown by numerous experiments, and, however completely the particles of the chemically active pigment may be covered by an oil film, they will necessarily come in contact with moisture — will decompose the water and absorb its oxygen, and convey it, together with the hydrogen, to the surface of the iron to cause rust.¹ For this reason the ideal paint for a steel or iron bridge should not contain a chemically active pigment, nor any strongly oxidizing agent in the way of driers.

We have also seen that linseed oil is permeable to moisture and to the gases and steam from locomotives. This was first clearly demonstrated, we believe, by Dudley, and to this fact may be ascribed the corrosion of the metal under an apparently intact coating of paint. It is true that in the mixture of oil with pigment in a very finely divided form, the tendency is for the pigment particles to more or less fill up the interstices in the oil film and render it less porous. How completely this is done depends more or less upon the shape of the minute particles of pigment, and, as Robert Job demonstrated in a paper read before the Franklin Institute of Philadelphia, it depends even more largely upon the fineness of grinding of the pigment particles. The finer the pigment is ground, the more perfect will be its protective power. This was shown very clearly by examination of the paint film under the microscope as well as by actual service test.

Paint Coatings Used at Panama. — At Panama, up to the beginning of the American engineering regime, the isthmus resembled a vast junk shop, where millions of dollars' worth of metal could be seen in various stages of oxidation and decay.

Little evidence was left to show that paint had been applied to most of the structural and fabricated metal used by the French

¹ This article was written without reference to the electrolytic explanation of corrosion, and is included here to show that independently of the theory engineers were beginning to recognize that pigments enveloped in oil were capable of stimulating corrosion.

engineers. Some of the old locomotives, however, used by the French were pulled out of the mire and found to be in fairly good condition. Sections of the paint still adhering were removed by Speller¹ and, upon his return to the United States, analyzed and found to consist largely of zinc, lead and small percentages of oxide of iron used probably as a coloring material. The analysis of some of these paints appears below, and would almost seem to indicate that the French possessed years ago, some knowledge of the inhibitive properties of pigments.

	No.	White Lead	Oxide of Zinc	Silica	Alumina	Oxide of Iron	Oil and Undetermined matter
White Paint	PIA	66.30	12.10	11.14	5.21	2.81	2.44
White Paint (Exca- vating Machine) . .	PIC	58.01	28.38	2.27	8.42	1.12	1.80
White Paint (La Boca)	PID	37.86	13.67	37.12	6.84	1.66	2.88
		Red Lead	Carb. of Lead				
Red Paint (French Locomotive)	PIB	70.06	11.90	3.18	5.10	5.86	3.90

Recent progress in the art of compounding protective coatings makes it possible to design paints superior to the above, and it is probable that in the future the problem of protecting the iron work at the canal zone will not be found as difficult as it has been in the past.

It should be remembered, however, in this connection that the metal used by the early French engineers and contractors was superior in quality to much of the metal that is in common use to-day. The authors must reiterate their opinion that the problem of protecting iron and steel depends largely upon the rust-resisting quality of the metal to be protected.

Painting Various Municipal Accessories, etc. Iron poles for trolley wires are sometimes imbedded in the earth after receiving a coat of tar. The upper part is then painted. The addition of lime to the tar used in painting the lower part of the poles is to be advised; in fact the addition of 20 per cent. of dry lime to the earth used in tamping around the pole will furnish some protection to the metal.

¹ Published by permission of F. A. Speller, National Tube Co.

The paint for the upper part of the poles should be inhibitive. Carbon paints, which have been so largely used for this purpose, in the authors' opinion are generally stimulative in their action and should not be used unless on top of a good inhibitive primer.

Lamp posts and letter boxes, which in the past have been painted with aluminum paint (a mixture of aluminum and zinc alloy powder suspended in bronzing liquid or collodion lacquer) have rusted rapidly. The vehicles of such paints are generally poor excluders and allow the moisture to get through to the metallic powder spread over the iron surface of the box or post. The metallic powders, being good conductors of electricity, inevitably lead to stimulated corrosion, for reasons which have been fully discussed in previous chapters.

Proper protection of lamp posts, boxes, and other articles of this sort, can best be secured by using a good inhibitive paint formula ground in oil with or without a percentage of varnish. A good bronze green, made from zinc oxide, white lead, zinc chromate, and willow charcoal, makes a most excellent coating for such work, both from a decorative and inhibitive standpoint. The use of red lead, provided it is inhibitive in its nature, for fire signal boxes is to be recommended. Another composition equally as good from an inhibitive standpoint may be made from bright red oxide of iron and basic chromate of lead, the latter possessing excellent inhibitive values.

Painting Refrigeration Machinery. — The painting of condensers and pipes for carrying brine has presented a problem that has puzzled the makers of the best paints upon the market. Instances of the complete failure of several different types of paint tested on this class of work have come to the attention of the authors who have recommended the application of a special formula for this purpose. The formula which has given the best results is made of asbestine, willow charcoal, red lead and zinc chromate ground in oil containing forty per cent. of a high-grade kauri gum varnish. The wonderful results obtained with this inhibitive paint, which has withstood the formation upon its surface of nearly two inches of salty ice for over a year, only adds to the weight of the plea that has been put forward in successive chapters in this book, namely, that both the pigment and the vehicle should be given consideration from the standpoint of inhibition, excluding value and moisture-resisting properties.

Ornamental Iron Work Protection.—For the protection of iron grill work, porch railings, etc., etc., the Bower-Barff and Wells processes have to some extent been successfully used, but the great majority of material of this kind must depend upon paint coatings for its protection. Red lead is very generally used for prime coating, and if inhibitive in nature serves the purpose well. In many cases the iron decoration of buildings has been painted a flat black, using lampblack in oil thinned with a large quantity of turpentine for flatting. The rapid evaporation of the turpentine leaves a porous surface. The unsightly rusted condition of much of this sort of work is a matter of common observation. If flat black is required for the finish, it should be put on over a good inhibitive primer.

CHAPTER X

THE TESTING AND DESIGN OF PROTECTIVE PAINTS

The Testing and Design of Paints. — Spreading value should, of course, receive careful attention in the selection of a protective paint, but this should not be allowed to be the first consideration. A paint that has a high spreading value would seem from one point of view to be the most economical, but if it fails to provide protection it will prove much more expensive in the end. No one knows this better than the painter, who is called upon to labor over rusted surfaces before repainting. Within reasonable limits, the paint that gives the best protection is the cheapest paint to use, no matter what its first cost may be. In order to determine in advance the efficiency of a paint, designed to protect iron from corrosion, recourse must be had to some form of preliminary test. In the following paragraphs the authors have endeavored to present a description of a number of such tests that have been proposed and used by various authorities, together with some directions which have a general bearing on protective paint testing.

General Directions in Regard to Testing. — When a series of commercial paints are to be tested in the field for their relative merits, it is well to use both the definite and indefinite spreading rates, making two sets of tests. For instance, if there is submitted for test six samples of paint, designed for the protection of iron, two steel plates should be used for each paint. The plates should be either sand-blasted or pickled in acid, and properly prepared for the test, as previously outlined.¹ One plate should be painted with the quantity of paint demanded by the surface. The operator should, of course, properly brush the paint out and not leave too much upon the surface, otherwise wrinkling will ensue. The other plate should be painted with just the number of grams of paint that is required to produce a spreading rate of say 900 square feet, if this rate is adopted. Great care should be taken to have the same operator apply

¹ See p. 180.

each paint tested, so that no great variable will be introduced in the preparation of the plates. The value of such tests is added to by including plates covered with the ordinary black mill-scale, as most structural steel is painted in this condition. Positive information may be obtained regarding the value of a paint when the tests are made upon both cleaned and uncleared plates, as above outlined, and with definite and indefinite spreading rates.

If the purchase of large amounts of paint is under consideration, samples should be submitted to the chemist for examination. If no specifications have been laid down for the composition of the paint, the chemist, if he so desires, may omit the analysis of the paint and may then proceed with the accelerated laboratory tests that are best suited to each paint, according to the purposes for which it is to be used. The results of the acceleration tests may be taken as fairly good evidence of how the paint will work in practice, but a series of practical exposure tests should also be started so that definite knowledge can be obtained in regard to their protective value.

Throughout such tests the greatest care should be taken that the number of grams of paint applied to each panel is recorded, and when reporting on the value the number of grams of paint should be calculated to the spreading rate per gallon, so that the final report will include this factor.

When testing pigments, if the proportions of pigment to vehicle, according to specific gravity, as used in the Atlantic City tests, are not satisfactory to the mind of the engineer making tests of this nature, the following method may appear more practical.

The pigments should be ground in well-settled raw oil, the amount of oil being regulated according to the amount necessary to form a medium paste with the pigment. This paste should readily break up for thinning, by the addition of more oil, so that the final product will be in the proper condition for brushing, without leaving streaked marks upon the plate. For instance, 91 lbs. of white lead requires 9 lbs. of oil to make a grinding paste. The subsequent addition of 31 lbs. of oil and 2 lbs. liquid drier prepares the composition for the brush. Eighty-four lbs. of zinc grinds with 16 lbs. of oil to a medium paste, which may be thinned with 60 lbs. of oil and 4 lbs. drier to brushing consistency. In the case of lampblack, 25 lbs. of the pigment require 75 lbs. of oil to grind to a paste. The addition of 100 lbs. of oil is necessary to form

a paint thin enough to apply to steel. After the oil has been added for the necessary flowing consistency a small amount of drier, generally about 12 to 15 lbs., should be added, in proportion to the nature of the pigment, which invariably affects the drying. For instance, in a paint high in lead and zinc, small quantities of drier are sufficient, whereas a paint containing lampblack or carbon black requires a large amount of drier.

In nearly all exposure tests which have been recorded the pigments have constituted the variable, while the vehicle has been kept as constant as possible. There can be no doubt of the fact that more information is needed in regard to different combinations between varied vehicles and the principal pigments.

Laboratory Acceleration Tests.—Laboratory tests to determine the protective power of pigments are of great value provided they can be depended on to furnish advance information in regard to the probable action of a given paint compound. A great deal of work has been done along this line. In 1896, Smith carried out a series of tests to determine the value of various pigments, by boiling them in water contained in small iron cups, and observing the rate of corrosion. Other tests have been used, of a similar nature.

Small iron cups painted on the inside have been filled with water, either pure or containing impurities, so as to approximate the action of the water or gases that the coatings would be exposed to in service. The liquid is allowed to evaporate, sometimes with the aid of heat, the cups are then again filled and the operation continued in this way for some time. Observations are made from day to day, to see whether rusting is taking place, and a careful record of the first and successive breakdowns is made.

A valuable apparatus for testing the value of paints which are to be submitted to alternate exposure to liquids and atmospheric gases was designed by Norton. It may be constructed from a box about 6 feet long, 2 feet wide, and 2 feet deep. In the middle of each end, on the top of the box, 2-in. steel collars may be placed to accommodate a 2-in. wood rod. Upon this rod may be placed a series of iron plates or disks, less than 24 inches in diameter, painted with various paints, and punched in the middle so that they will slide along the rod. These plates are kept about 2 inches apart, when making the test. The box is then half filled with the liquid, which may be salt water, alka-

line, or acid water. By mechanically turning the rod, the plates are kept slowly moving through the liquid in which they are half submerged. The test may be kept up for several weeks. The alternate exposure is severe, and some paints last in this test but a short while.

Another method, which is satisfactory for large samples, is the acceleration test box, devised by one of the authors, for testing painted surfaces in an artificial atmosphere, containing various percentages of carbonic acid gas, ammonia, etc., duplicating atmospheric conditions in those localities in which the paint is to be used. This box may be also used for testing various steels, for their resistance to corrosion. The box is about four feet long, 2 feet wide, and 2 feet deep, and is fitted with glass sides and top. The top of the box contains a row of girders, from which the samples are suspended from small hooks. The side of the box is fitted with a tubular opening, through which carbon dioxide may be passed. Water is kept in a tray at the bottom of the box, and thus the atmosphere of the box is kept constantly humid. The temperature of the box may be adjusted to suit the requirements of the test. Ozone may be developed with a Ruhmkorff coil and sparker. In fact, any desired atmosphere can be introduced into the box. Samples of painted surfaces exposed to this test have failed in a remarkably short time.

Another acceleration test has been proposed by Loesner, and is described in Andes' work on Iron Corrosion, as follows: "When the plates of sheet iron are coated with paint, rust forms — as is well known — on the surface of the metal after a short time. Owing, however, to the slowness of the reaction, immersion in water does not afford a suitable means for determining the durability of paint, whereas, on the other hand, steam places a very convenient method at our disposal for this purpose. With this object, plates of sheet iron are cleaned perfectly bright on one side, by means of emery paper, the clean surfaces — which must not on any account be touched with the fingers — being then coated over with a thin uniform layer of the paint to be tested, and left to dry at the ordinary temperature for four days. The plates are next set, painted side downwards, over a boiling water-bath, so that the surface of the paint is just 2 inches (5 cm.) above the constant level of the water. At the end of fifteen hours, the plates are dried for a short time at 100° C. (not higher), and the

layers of paint impregnated with aniline oil applied with a soft brush. Being thus softened they can be removed, and the metal is then dried by means of alcohol. For the paint to be classed as good, the metal must have remained perfectly intact, a condition readily recognized by the appearance of the scratches formed on the surface by the emery paper used in the initial cleaning. Many paints will stand this steam test after the painted iron has been heated to 100° to 105° C. for about five hours."

A novel method for testing the pigment portion of paints, to determine whether the pigment is inhibitive or stimulative, was developed by one of the authors during his researches. The pigments to be tested are rubbed up with sufficient water to make thick water-color paints, and are then flowed or brushed upon the clean blades of steel table knives. After the coatings are dry the knives are laid on a wet blotter and covered with a sheet of wet blotting paper. At the end of forty-eight hours the surfaces are cleaned off with running water and a stiff brush. This acceleration test has been found to give results which agree with the oil film tests.

The appearance of the knife blades after being used in this test is shown in Fig. 68*a* and *b*.¹

Perry developed the foregoing test so that it could be made applicable to the examination of paints ground in oil. He recommends that a portion of the paint when it is received for examination be placed in a test tube and shaken several times with benzine, in order to extract the vehicle, the extractions being disregarded and the separated pigment used for the test. Small centrifugal machines for the accommodation of the test tubes may be used for the extraction. The pigment is removed from the test tube and placed upon a sheet of druggists' filter paper. It is then moistened and with the finger rubbed to a soft paste. A razor blade, or other small piece of steel highly polished, is then covered with the paste together with the paper, and laid upon a porcelain dish within a cigar box. Several different pigments may be tested in the same way and included in the same box. The box is kept constantly humid by lining the sides and top with druggists' filter paper kept constantly moist with

¹ One of the authors has recently devised a new form of acceleration test which promises to give valuable results but which has not been sufficiently developed to publish.

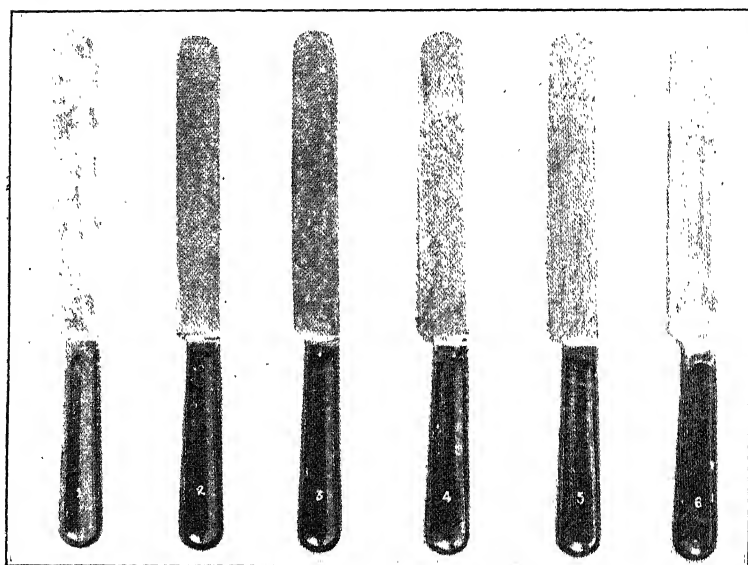
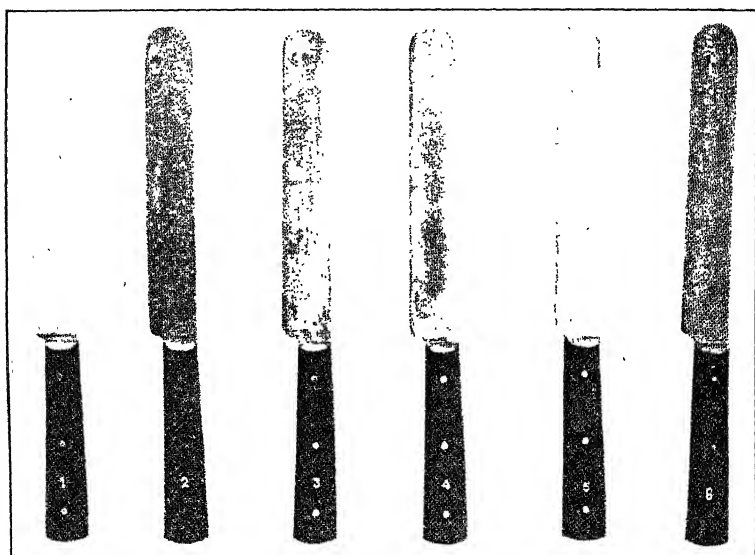


FIG. 68a and b. — Showing the appearance of knife blades used in Cushman's test.

water. At the end of a few hours the box may be opened and the steel plates removed from their wrappings of paper and pigment. After washing and scrubbing with a tooth brush, in order to remove any pigment which persists upon the metal, the amount of corrosion which has taken place may be easily ascertained. Another acceleration test which gives valuable information has recently been devised by one of the authors, but as the work was done in a government laboratory and has not yet been published, it cannot properly be included here.

It is natural that there should be considerable difference of opinion among both paint manufacturers and consumers in regard to the value of acceleration tests. It is noteworthy that the same discussion has been going on for years in regard to Portland cement, and yet all cement is bought and sold subject to acceleration tests. It is the authors' firm conviction that the same conditions will eventually be developed in the purchase of protective paints. Extravagant claims made by manufacturers will not always satisfy the consumer, and "best by test" will inevitably replace "best by claim." There are perhaps a thousand "best" protective paints in the market, and among them the consumer is at present at a loss to decide. In no section of technical industry are standard tests more necessary than in the one under discussion here.

Design of Protective and Inhibitive Paint Coatings. — In the manufacture of paints, the various pigments are usually ground in oil to a paste, and stored away in that form in mixing tanks. This practice is followed by the larger manufacturers who have the proper facilities. When an order is received for any special combination, the proper weights of each paste, according to the percentage composition of the paint desired, are mixed together and thinned with the necessary amount of oil and drier. For instance, if a white paint was desired for iron and steel, and, in the judgment of the engineer ordering the paint, the following composition was considered best to use in the locality where the work was to be done:

Pigment Composition

Basic Carbonate — White Lead	67 per cent.
Zinc Oxide	20 per cent.
Asbestine	3 per cent.
Calcium Carbonate	10 per cent.

with this working formula the paint-maker could proceed with the manufacture of the product. If about five gallons of this paint was desired, the following amount of paste would be used, these amounts being proportioned to the percentage composition of the mixture:

42.5 lbs.	Basic Carbonate — White Lead in Oil
14.2 "	Zinc Oxide in Oil
3.3 "	Asbestine in Oil
6.6 "	Calcium Carbonate in Oil
20.6 "	Raw Linseed Oil ($2\frac{2}{3}$ gals.)
1.25 "	Drier ($\frac{1}{8}$ gal.)
.5 "	Turpentine ($\frac{1}{12}$ gal.)
88.95 lbs.	

Weight per gallon, 16 lbs., 5 oz.

Analysis of this paint would show the following composition:

	Per Cent. in Pigment	Per Cent. in Vehicle	Per Cent. in Total Pigment and Vehicle
Basic Carbonate—White Lead ...	67.01	42.84
Zinc Oxide	19.89	12.71
Asbestine	3.86	2.47
Calcium Carbonate.....	9.24	5.91
Raw Oil	94.30	34.02
Drier	3.89	1.40
Turpentine	1.81	.65
	100.00	100.00	100.00

This paint could be tinted to any color desired. For instance, 100 lbs. of the white base could be tinted with 5 lbs. zinc chromate, in order to get inhibitive yellow paint, or with 3 lbs. of a good inhibitive black pigment, in order to secure a good gray tint.

For special formulas, however, the pigments specified in the formula are generally weighed out in their proper proportion and mixed and ground in linseed oil. If the formula called for 200 gallons of green paint, and the pigment specified was as follows:

Special White	52 per cent.
Silica	22 per cent.
Zinc Yellow	7 per cent.
Medium Chrome Yellow	8 per cent.
Prussian Blue (Inhibitive)	6 per cent.
Whiting	5 per cent.

this could be made by weighing out the following amounts of pigments in oil, mixing and grinding:

750.0 lbs.	Special White
312.5	Silica
112.5 "	Zinc Chromate
125.0 "	Neutral Lead Chromate
87.5 "	Prussian Blue (Inhibitive)
62.5 "	Whiting
600.0 "	Raw Oil
<hr/>	
2050.0 lbs.	

This paint could be thinned for application with:

2050 lbs.	of above paste
100 "	Drier
850 "	Raw Linseed Oil
3000 lbs.	

This paint would weigh about $12\frac{1}{2}$ lbs. per gallon.

Inhibitive Paint Formulas.—The authors have frequently been asked to design protective and inhibitive paints for special purposes.

While it would appear unwise for the authors to attempt standardization of paint formulæ, or to define the percentage composition of paints intended for iron and steel, it is believed that to give the formulæ of a few paints which have proven of value in field tests would be a matter of interest to the manufacturers of protective coatings, as furnishing a basis upon which to make further tests. In various parts of this book there has been given a general outline of the composition of paints of especial value for special purposes. The following formulæ would be of value for general use on iron work:

BROWN-ZINC

Metallic Brown (neutral).....	60 per cent.
Zinc Lead.....	20 per cent.
Zinc Oxide.....	20 per cent.

CHOCOLATE COLOR

Metallic Brown (neutral).....	90 per cent.
Willow Charcoal	5 per cent.
Zinc Chromate	5 per cent.

RED

Bright Red Oxide (free from acid or sulphur)	95 per cent.
Zinc Chromate	5 per cent.

RED

Bright Red Oxide.....	65 per cent.
China Clay.....	15 per cent.
Red Lead	15 per cent.
Zinc Chromate	5 per cent.

BLACK

Willow Charcoal and Bone Black	68 per cent.
Zinc Chromate	2 per cent.
Inert	30 per cent.

STEEL-BLACK

Sublimed Blue Lead	60 per cent.
Willow Charcoal	20 per cent.
Inert	20 per cent.

GREEN

Zinc Oxide	45 per cent.
Sublimed White Lead	25 per cent.
Inert	15 per cent.
Zinc Chromate	5 per cent.
Inhibitive Prussian Blue	5 per cent.
Medium Chrome Yellow.....	5 per cent.

GREEN

Inhibitive Prussian Blue	4 per cent.
Zinc Chromate.....	3 per cent.
Chrome Yellow	8 per cent.
Asbestine	15 per cent.
Zinc Lead or Zinc Oxide and Corroded ¹	
White Lead	70 per cent.

WHITE

Zinc Oxide	60 per cent.
Corroded or Sublimed White Lead	30 per cent.
Asbestine	10 per cent.

WHITE

Zinc Lead.....	20 per cent.
Zinc Oxide	20 per cent.
Corroded or Sublimed White Lead	50 per cent.
Kaolin or Silica	10 per cent.

¹ If corroded lead is used, it must be in small proportion on account of its action on the green.

Wire Fence Paint. — On the wire fences at Pittsburg several paints of the inhibitive and stimulative pigment types were tested. Excellent results were obtained with the use of a paint of approximately the following composition:

Natural Bright Iron Oxide	65 per cent.
Silica.....	20 per cent.
Willow Charcoal	5 per cent.
Red Lead	5 per cent.
Zinc Chromate	5 per cent.
	<hr/> 100 per cent.

This paint, ground in oil alone, would afford good protection to wire, but when ground in a vehicle of the following nature, it would prove of even more value:

Boiled Linseed Oil.....	23 per cent.
Raw Linseed Oil	45 per cent.
Kauri Varnish	20 per cent.
Turpentine and Drier	12 per cent.
	<hr/> 100 per cent.

Another paint showing good results on the Pittsburg wire fences was of the following composition:

Zinc Chromate	90 per cent.
Inhibitive Prussian Blue.....	10 per cent.
	<hr/> 100 per cent.

This paint, however, is quite expensive on account of the large percentage of zinc chromate.

The carbon black and graphite paints applied to the wire fences showed very bad results, corrosion becoming apparent within six months after their use.

Condenser Paint. — The use of a formula of the following composition will be found of value in painting condensers and pipes subjected to low temperatures:

PIGMENT	
Willow Charcoal or Drop Black	40 per cent.
Red Lead	25 per cent.
Asbestine and China Clay.....	30 per cent.
Zinc Chromate	5 per cent.
	<hr/> 100 per cent.

VEHICLE

Boiled Linseed Oil	20 per cent.
Treated China Wood Oil	20 per cent.
Raw Linseed Oil	50 per cent.
Turpentine and Drier	10 per cent.

 100 per cent.

Or the Boiled Linseed Oil and China Wood Oil may be replaced with Copal Varnish.

Paint for Iron Piping. — A paint that would prove efficient for use at the seashore for protecting piping exposed to the weather, could be made of the following composition:

White Lead	55 per cent.
Zinc Oxide	20 per cent.
Silica	10 per cent.
Willow Charcoal	10 per cent.
Zinc Chromate	5 per cent.

 100 per cent.

Formula Labeling. — The purchasing agent of the large corporation is often at a loss, when buying paint, to know whether he is securing that grade for which he has contracted. The labeling of house paints in various States by certain manufacturers was brought about by legislation as well as by a desire for honesty. The analysis printed upon the label is generally considered as an evidence of the manufacturer's desire to make a good paint, otherwise the analysis would not appear. Formula labeling on paints for iron and steel may come in the near future, and such an innovation will probably be welcomed by the engineer, architect, purchasing agent, and consumer.

CHAPTER XI

THE PROPERTIES OF PIGMENTS

The Requisites of Protective Coatings. — Although this book deals largely with paints for the protection of steel and iron, the wide interest of late that has been exhibited by the engineer, regarding the composition and value of various paints, demands that a brief description of the physical properties of pigments and the prime requisites of paints should also be included.

A proper understanding of certain basic laws regarding materials for the fabrication of protective coatings is absolutely essential to the factory superintendent or chemist who is called upon to specify paints, and should also be of interest to the painter, architect, and engineer who constantly use and depend upon these products.

Meaning and Cause of Hiding Power. — Structural material of various kinds differ in the demands made upon the paint used for their protection and decoration. That the film should have proper covering and hiding power, or opacity, is essential. Opacity in a paint is dependent upon the difference in the refractive indices of the pigment and the vehicle with which the pigment is mixed. The farther apart the indices of refraction of the composite pigment and the vehicle, the greater the opacity. Greater protection from the powerful rays of the sun is afforded the structural material upon which opaque paints are applied. Proper hiding of the surface is necessary from a protective as well as a decorative standpoint.

Whiteness. — White pigments should not darken when made into paint. White lead, zinc oxide, and barytes are all examples of white pigments, which when ground in oil produce white paints. The barytes in such a formula becomes transparent in its oil coating, but has no darkening influence on the composition.

Lithopone, when ground in oil and painted out, gives a whiter surface than any other pigment. For outside work, however, it is not well suited on account of its liability to turn dark. Zinc

oxide is generally taken as a standard of whiteness, and is used for comparison with various other pigments when determining their degree of whiteness.

Stable and Chemically Active Pigments. — Pigments are sometimes classified according to their behavior in oil, as "*chemically active*," or "*inert*." The term "inert pigments" generally applies, however, to that group of pigments which when ground in oil show relatively slight opacity but extreme stability toward the oil. There are some white pigments which are of great value for their hiding power and other properties, but which, because of their basic or alkaline nature, show chemical activity towards the oil in which they are ground, causing saponification, and final disintegration of the paint film. Such pigments are chemically active, and are often the cause of chalking, checking, and discoloration.

Spreading Value. — The number of square feet over which a paint is spread is an important consideration. Some pigments in oil have a relatively low, while others have excessive spreading quality. Too high-spreading quality causes the formation of thin films which do not properly resist the action of the elements. A number of authorities believe that a combination of pigments, in proper percentages, of both types, gives a paint of improved spreading quality, and makes it easier to produce a film of the proper thickness.

Effect of Gases on Paints. — Some pigments are not affected by sulphurous gases, while others darken under such exposure, and are materially changed in color. Zinc oxide and basic sulphate-white lead are good examples of base white pigments upon which sulphur gas has practically no effect, while basic carbonate-white lead is an example of a pigment easily affected, the black sulphide of lead being the product formed.

Paint Coat Strengtheners and Preventives to Settling. — Magnesium and aluminum silicates (asbestine and talcose) have been suggested and much used for reinforcing paint coats. These pigments, the former in needle-shaped particles, and the latter in flake form, are believed by many authorities to possess value in overcoming the defects of certain prime white pigments when used in too large a percentage. It is claimed that they not only increase the abrasion resistance of the film, but render it much stronger. They are also largely used by the paint manu-

facturer to-day as anti-settlers, as they have the property of holding up heavy pigments and preventing the settling and hardening of paints in which they are used. The holding up or non-settling property of paints is vitally necessary. Anti-settlers should be used with moderation, however, as excessive use may be considered an adulteration.

Excluding Properties and Elasticity. — A paint coating for iron should possess the property of being an excluder of moisture. It should be impervious to rains and storms. It should also possess enough elasticity to conform with the expansion or contraction of the materials upon which it is used. This elasticity is largely dependent upon the proper regulation of the percentages of pigments contained in the paint. Linseed-oil films are very elastic, but through progressive oxidation they soon become deficient in this property, whereas linseed-oil films, containing various pigments in the proper proportion, maintain their elasticity and increase in tensile strength.

That the pigments which go into the formation of a paint should be of different sizes, is the conclusion of Perry¹ in his elaborate researches upon the physical properties of paint films. Following is a brief résumé of the work of this authority: — The law of minimum voids which applies to concrete also applies to a paint coating. The pigments which are made by sublimed processes are extremely fine, and serve the same purpose as sand in concrete, while pigments coarser in nature are comparable to the broken stone or rock. The use of asbestine has been likened to the use of reinforcing rods and wire mesh in concrete, and adds strength to the paint coating. — If Perry's conclusions are accepted, it is evident that a paint, made by combining in certain percentages pigments of each type, is far superior to a paint made of one single pigment.

Working Properties of Paints. — The so-called tooth of pigments is a term applied by the master painter to paint which works well under the brush, and gives proper penetration without too much slipping greasiness or excessive flow. The use of pigments, such as silica and silicates and barytes, gives this so-called tooth.

In concluding this general and brief discussion of the properties of pigments in their relations to paint films, the authors have

¹ The Physical Properties of Paint Films.

endeavored to present all statements made, from an unbiased point of view. There are a number of paint authorities who believe that a paint compounded of a single good pigmentary substance, and an efficient vehicle provides as adequate protection as it is possible to obtain. While not agreeing with these authorities, the writers believe that their views should be given the fullest consideration. In the course of time thorough testing will remove these varying opinions from the realm of theory to that of fact.

Description of Pigments in General Use for Painting Iron. — The following descriptions of the properties of the various pigments is given with a view of presenting information in a concise form, which it is believed will be useful to many persons on whom the responsibility for protective paint design falls.

Basic Carbonate-white Lead. — Basic carbonate-white lead is made by several processes:

- The Old Dutch Process;
- The Carter (or Quick) Process;
- The Precipitation Process;
- The Electrolytic Process;
- The Mild Process, etc.

In the Old Dutch Process, pure lead buckles are placed in clay pots with dilute acetic acid, the pots being subsequently stacked up and covered with boards and tan bark. The fermentation of the tan bark raises the temperature and causes the formation of carbon dioxide, which acts on the acetate of lead formed within the clay pots, producing a basic carbonate of lead. After two months or more the action is completed and the white lead is broken up, ground in water, floated to separate the "blue" or uncorroded lead, then dried in copper pans. It is sold dry or ground in oil.

In the Carter Process, the lead is made in two weeks by acting upon finely atomized lead particles with dilute acetic acid and carbon dioxide gas (the latter generated from burning coke) within large revolving cylinders.

The Mild Process uses no acid, depending upon the oxidation effect of air blown upon finely divided particles of lead, agitated in water. The hydrate of lead thus formed is subsequently carbonated. This material does not require the washing necessary for lead made by other methods of manufacture, as it contains no free acetic acid.

By the above processes, a white product having the composition $2\text{PbCO}_2 \cdot \text{PbOH}_2$, is formed, generally containing about 85 per cent. PbO , and 15 per cent. carbon dioxide and water. It is soluble in dilute mineral acids or acetic acid. The acetic acid solution is generally used for the assay of white lead, and may be precipitated as lead chromate with standard volumetric bichromate solutions. Lead salts may be precipitated with hydrogen sulphide, to form the black sulphide of lead, and this reaction is also used in analytical work. All forms of basic carbonate-white lead are easily reduced to metallic lead, by the use of the blow-pipe, in the presence of a reducing substance such as charcoal.

Basic carbonate-white lead has a specific gravity of 6.8, and grinds in 9 per cent. of oil to a stiff paste. It may then be thinned to a working consistency with 38 per cent. of oil. As generally reduced by the master painter, 100 lbs. are mixed with 4 to 6 gallons of oil, with the addition of one quart of turpentine and a pint of drier, the amount of oil or turpentine varying with the nature of the surface to be painted and the conditions prevailing. Basic carbonate-white lead is an extremely opaque pigment and possesses excellent body. It is somewhat deficient in spreading rate and is, therefore, generally mixed with zinc oxide or other pigments of high spreading values, when used for general painting purposes. It is easily affected and darkened by sulphurous gases, and should not be used with other pigments containing sulphur in any form.

It is claimed that on account of its alkaline nature it acts upon the saponifiable oil in which it is ground, forming lead soaps, which are the active cause of the chalking of white lead — the greatest evil attending its use. Solubility in carbonic acid of the atmosphere and decay in the presence of sodium chloride may be active causes of the rapid chalking of this pigment at the seashore. Checking in some climates appears to proceed rapidly on white lead, in a deep hexagonal form, leaving a series of rough crests and cracks. This checking is secondary to the chalking which takes place.

It generally has inhibitive tendencies, and is a valuable constituent of certain paints intended for the protection of iron and steel.

Landolt¹ says: "White lead, used alone and in a pure state,

¹ Iron-Corrosion and Anti-Corrosive Paints. L. E. Andes.

is not a good paint for iron-work. Apart from the fact that the pure white of the pigment will speedily become impaired and dirty, the paint also sets hard in a short time, the elasticity disappears, and cracks are formed. For this reason white lead is mixed with other substances, in the first place to impart color to the paint, and furthermore for the purpose of increasing its power of absorbing oil, this latter, or linseed varnish, being the principal agent determining the durability of the coating.

"The more oil required by a pigment in order to produce a distributable paint, the better will it be adapted for use on iron, especially in the open air, provided it satisfies the other conditions, of covering power, neutrality, and capacity of resistance to acids."

Zinc Oxide. — Zinc oxide is a very valuable prime white base pigment, the larger quantity being produced by the roasting and sublimation of Zincite and Franklinite, the latter being found in large quantities at Franklin Furnace, New Jersey. The New Jersey zinc oxide runs about 99 per cent. pure, while that produced in Wisconsin contains upward of 5 per cent. of lead sulphate.

Another variety used, and which is usually about 99.5 per cent. pure, is produced by the sublimation and oxidation of spelter, this variety being the standard for whiteness, and known as French Process Zinc Oxide.

This pigment has a specific gravity of 5.2, and grinds in about 16 per cent. of oil to a stiff paste, 100 lbs. of which may be thinned for application with 64 lbs. of oil. It is a very opaque pigment, and possesses excellent spreading properties, being used in admixture with basic carbonate-white lead for outside paints. Being a very white fine pigment by nature, it acts well with the lead pigments, and helps to overcome the chalking tendency which the latter may possess. Because of its stable nature, and extreme whiteness, it is an excellent base for delicate colors, bringing out their purity of tone. Zinc oxide has good drying properties of itself, but the use of litharge aids its drying and is the safest kind of drier to use with this pigment. Progressive oxidation gives zinc oxide a hard surface, and consequently does not resist the changes in temperature as well as when in combination with a softer pigment. Zinc oxide is invaluable as a pigment base for enamels, being possessed of great body and whiteness, and giving a high, permanent gloss when ground in varnish. The checking

of zinc oxide is very regular and characteristic, being of a distinct triangular form. Nearly all zinc oxides are fairly good inhibitive pigments.

Zinc oxide is soluble in most mineral acids to a clear solution. Solutions of zinc oxide in acetic acid may be titrated with standard ferrocyanide of potash solutions, this being a quick volumetric method used in its determination. Solutions of zinc may be precipitated with sodium carbonate, and the white zinc carbonate thus formed ignited to the oxide and weighed as such.

Basic Sulphate-White Lead (Sublimed White Lead). — Basic sulphate-white lead (sublimed white lead) is made from galena, an ore containing a very high percentage of sulphide of lead. This ore is mixed with fuel, placed in furnaces, and volatilized. The fume is brought into contact with air, and becomes oxidized to a basic sulphate of lead. The fumes are then drawn through flues and air-cooled pipes to bags or receivers.

Basic sulphate-white lead is an amorphous pigment, of great fineness, and almost of the same characteristic whiteness that is exhibited by basic carbonate-white lead. It has a specific gravity of 6.2, and grinds in about 10 per cent. of oil to a stiff paste that may be thinned for application, to brushing consistency, by the addition of 38 per cent. of oil to 100 lbs. paste.

This pigment possesses extreme chemical stability, and is not subject to the blackening caused by sulphurous gases, as is the case with some pigments. Delicate colors, such as greens, blues, and yellows, may be mixed with this pigment without any action on the color. This stability renders it invaluable for many tinted paints.

The tendency of certain lead pigments to liver or become thick in cold weather is often due to the presence of sulphites, but a pure basic sulphate-white lead, free from sulphites, does not exhibit any great amount of stiffness under the brush during cold weather.

Commercial basic sulphate-white lead usually runs very uniform in its composition, analysis showing it to contain approximately 70 per cent. of lead sulphate, 20 per cent. of lead oxide, and 5 per cent. of zinc oxide. The lead sulphate is chemically combined with the lead oxide, forming a stable and definite chemical compound. An examination of the pigment under the microscope shows absence of crystals, thus proving that the lead

oxide present is chemically combined and not in its regular crystalline form. Lead oxide is insoluble in ammonium acetate, but when chemically combined with lead sulphate it readily goes into solution when treated with ammonium acetate. This solubility of basic sulphate of lead is utilized by the analytical chemist in the detection, separation, and estimation of sublimed white lead in mixed paints.

Sublimed Blue Lead. — Sublimed blue lead is made by burning coarsely broken lumps of galena, admixed with bituminous coal, in a special form of furnace. The fumes which are volatilized from this mixture are very complex in their chemical make-up, and in color are white, blue, and black. After being drawn through the cooling pipes by the suction of huge fans, whereby the fumes are cooled, the pigment is deposited in bags. This pigment is bluish black in color, and has been highly recommended for use on iron and steel. Its composition runs approximately as follows:

Lead Sulphate	50 per cent.
Lead Oxide	35 per cent.
Lead Sulphide	5 per cent.
Lead Sulphite	5 per cent.
Zinc Oxide	2 per cent.
Carbon	3 per cent.

The color of the pigment is largely due to the carbon and the lead sulphide. Its specific gravity is 6.4, and it grinds in 10 per cent. of oil, to a stiff paste, 100 lbs. of which may be thinned with about 26 lbs. of oil to working consistency. Some manufacturers use it in mixture with iron oxide and other pigments for the production of paints for metal surfaces. Wood and others have found it of value for this purpose. It has a tendency to chalk, but this may be overcome by admixture with other pigments such as zinc oxide and iron oxide. Lane has found it of especial value admixed with lampblack.

The selection of this, as well as all other pigments, should, in the authors' opinion, be decided by tests, and as far as possible by the observation of its protective action under service conditions.

Lithopone. — Lithopone is probably the whitest pigment known, and is extremely desirable for the manufacture of high-grade enamels, the amount consumed for this purpose being very

large. It is manufactured by the double decomposition of zinc sulphate and barium sulphide, two soluble salts which interact to produce two pigments chemically combined, namely, zinc sulphide and barium sulphate. The resulting product is filter-pressed, and furnace-dried, after which it is rendered more opaque by disintegrating the heated pigment in cold water. It is afterward thoroughly washed, and again filter-pressed, then dried and ground. The production of this pigment is carried out in the factory under certain definite and critical temperatures. Proper control of the solutions for their purity and strength is constantly maintained, and the greatest care throughout the process is necessary in order to produce a high-grade product.

Although lithopone is a very stable pigment, it has very peculiar photogenetic qualities, and when exposed to the action of the actinic rays of the sun, in the presence of moisture, darkening of the pigment results. The pigment sometimes resumes its normal color, however, in a very short time after the darkening. In the absence of moisture, this darkening cannot take place. It is most excellently suited as a pigment for inside use, but for outside use it requires a very large percentage of some more stable pigment, such as zinc or calcium carbonate, in order to prevent this rapid darkening and to prolong its life.

Lithopone has a specific gravity of 4.25, and grinds in about 13 per cent. of oil to a paste that may be subsequently thinned with 60 lbs. of oil to 100 lbs. paste in order to form a paint of the proper flowing consistency. When spread, it shows high covering value and brushes exceedingly well. This pigment is sometimes a fairly good inhibitive pigment, but must be admixed with other pigments when designed for use on iron or steel, because of its rapid disintegration when exposed outside. Lead driers should not be used with lithopone.

Zinc Lead White.—This pigment is made by the reduction of sulphur-bearing ores of lead and zinc, in especially constructed furnaces. Volatilization of the lead and zinc, and subsequent oxidation, takes place, with the formation of a pigment fume consisting of about equal parts of zinc oxide and lead sulphate. The fume is cooled by passage through long metal pipes, and collected in bags. Subsequent treatment for whitening and desulphurization is then made, and the pigment as placed upon the market is extremely fine in its particle size.

This pigment has a specific gravity of 4.4, and grinds in about 12 per cent. of oil. It is a most excellent pigment for use in tinted paints, but is seldom used alone for white paints, because of a very slight yellowish tint. It has proved of considerable value when mixed with varying percentages of white lead and zinc oxide, and some inert pigments. In its chemical stability it resembles basic sulphate-white lead, and is very well suited for the manufacture of paints containing delicate colors, such as blues and greens. It is generally somewhat inhibitive, and in this case may be used with safety on iron and steel.

Leaded Zinc. — In manufacturing this pigment, various grades of lead and zinc ores are mixed, roasted, and furnaced. The fume therefrom is cooled through pipes, and collected in bags; the process in some ways resembling those used in the manufacture of zinc lead white and sublimed white lead. This pigment has a specific gravity of 5.8 and the analysis shows the presence of about 25 per cent. of lead sulphate and 75 per cent. of zinc oxide, with traces of zinc sulphate and sulphur dioxide. The product is a very stable pigment, resembling zinc oxide and zinc lead white. This pigment oftentimes contains a small percentage of zinc sulphate which may affect the life of the paint in which it is used. Zinc sulphate also has the effect of causing paints to liver to some extent. Because of the presence of a soluble salt such as zinc sulphate it must be used with care when intended as the basis of a paint for iron and steel.

Barium Sulphate (Barytes). — Barium sulphate, or barytes, is one of the most important pigments used in the manufacture of paints. It occurs as a mineral in large quantities and very widely distributed. In its preparation for the market, the mineral is ground, washed in acid to free it from iron and to whiten its color. It is then washed several times and dried. Flotation of the pigment produces a very fine grade. The pigment is used in large quantity as a base upon which to precipitate colors, and also together with other white pigments in the manufacture of ready-mixed paints. It renders the paint coating more resistant to abrasion, and gives to the paint certain very important brushing qualities. It is a very stable pigment, not being materially affected by either acid or alkali and can be used with the most delicate colors. In oil, it is transparent and must be mixed with opaque pigments when used in mixed paints. It is a very

heavy pigment, having a specific gravity of 4.4, and grinding in about 10 per cent. of oil. It is generally used with lighter pigments, such as asbestine, in order to prevent its settling.

Blanc Fixe is an artificial form of barium sulphate, made by mixing solutions of soluble barium salts with sodium sulphate or other soluble sulphates, causing precipitation of barium sulphate. This material has a somewhat lower gravity (4.2) than the natural barytes and does not have the same tendency to settle out when used in paints. This pigment is also used as a base for colors and also in ready-mixed paints, giving good brushing qualities to the paint. It has more opacity in oil than barytes and for some purposes is better suited than the natural form of barium sulphate. Both barytes and blanc fixe are liable to contain traces of acids or acid salts, and they must be carefully tested, before using in paints to be applied to iron or steel.

Gypsum (Calcium Sulphate).—Gypsum, or calcium sulphate, is found in nature very widely distributed. In its natural form it contains about 20 per cent. water of combination. It has come into wide use in the manufacture of various colors, and is often found in ready-mixed paints. It is a very stable pigment, and, although it lacks any hiding power in oil, when ground in water it is very opaque, and is largely used as a base for distemper colors. It is slightly soluble in water, however, and when present in a paint coating it is liable to leach out. It should never be used upon iron or steel, because of the corrosion which it is certain to cause, due to the ease with which it is ionized in the presence of water. It has a specific gravity of 2.3 and grinds in about 22 per cent. of oil. This pigment is present to a great extent in Venetian red.

Magnesium Silicate (Asbestine and Talcose).—This pigment comes in two forms: as asbestine and as talcose. The former is very fibrous in nature and is a very stable pigment to use in the manufacture of paint on account of its inert nature and tendency to hold up heavier pigments, and prevent settling. It also has the property of strengthening a paint coat in which it is used. The talcose variety is very tabular in form, and is also somewhat largely used in the manufacture of mixed paints. Both varieties are transparent in oil, and they are very inert toward iron or steel. They have a gravity of about 2.7 and grind in about 32 per cent. of oil.

Whiting (Calcium Carbonate). — Whiting, or calcium carbonate, occurs very widely distributed in nature, as chalk. After proper purification and grinding it forms a pigment with a specific gravity of about 2.8, which grinds in about 20 per cent. of oil. It is used largely in distemper work and also to a considerable extent in the manufacture of oil paints, being considered very valuable in small percentages in neutralizing any free acid contained in the linseed oil. It spreads very well and does not settle to any marked extent. The artificial, precipitated form of calcium carbonate is much lighter in gravity (2.5), and requires about 25 per cent. of oil for grinding. This form possesses more hiding power and, although it has a tendency to chalk, it is very valuable for certain purposes. The precipitated form should not be used in inhibitive paints, owing to the fact that it generally contains occluded impurities which tend to stimulate corrosion.

Aluminum Silicate (China Clay). — Aluminum silicate, or China clay, is a widely distributed pigment found in granitic formations. This pigment plays an important part in the manufacture of paints. It is a fine, amorphous, white powder, extremely permanent, and when ground in oil shows very little hiding property. It has a specific gravity of 2.6 and grinds in 28 per cent. of oil. It is a very stable compound, not being affected by ordinary acids.

Silica. — This is a most valuable white pigment, used in immense quantities for wood fillers, and in moderate percentages in mixed paints, both for iron and for wood. It is usually of great purity, often running over 97 per cent. SiO_2 , and when ground in oil becomes perfectly transparent. In combination with white lead and zinc oxide it produces a most excellent wearing paint, both for seashore and inland use. It has marked tooth and spreading properties. It is a good extender for iron and steel paints, and gives the coating a harder surface.

Litharge. — Litharge (PbO), or lead monoxide, in color is a yellowish red pigment, made by submitting metallic lead for several hours to oxidation under intense heat, in reverberatory furnaces. It has a specific gravity of 10 and grinds in about 9 per cent. of oil. It comes into large usage as a drier in the manufacture of boiled oil or japans. It is generally very inhibitive and gives a good, hard drying, elastic film.

Red Lead. — Red lead is a very heavy, brilliant red pigment,

made by submitting litharge to further oxidation in reverberatory furnaces. It has a specific gravity of 8.7. It varies in color and strength of tone, according to the degree of oxidation and physical structure. It is considered as one of the most valuable pigments known for the protection of steel and iron, and has been used for this purpose for many years.

Red lead is also produced by heating litharge with sodium nitrate, in large iron pots, the interaction taking place forming red lead and sodium nitrite, the latter being a very valuable salt in the manufacture of para reds. Red lead, when used pure, is almost always mixed at the time of application, the average formula being 30 lbs. of red lead to the gallon of oil. No drier is required, because of the rapid drying nature of the red lead itself. Because of the stiffness of red lead in oil and the difficulty in spreading a properly proportioned mixture, thinning with turpentine and volatile thinners is sometimes resorted to by workmen, causing a loss in the protecting value of the mixture. This pigment is more or less affected by sulphurous gases, under the action of which it turns brown. Admixture with certain inert pigments is to be recommended, in some cases. The inhibitive nature of red lead will vary according to the method used in its manufacture and the quantity and kind of impurities which it carries. It should always be tested, if possible, before its selection as a protective agent.

Orange Mineral. — Orange mineral is produced by the oxidation in reverberatory furnaces of white lead which is slightly off color. It is of the same chemical composition as red lead, but it possesses a different tone. Because of the tendency of oxides of lead in linseed oil to absorb oxygen, and cause stiffening and hardening of the mixture, these pigments are seldom used alone in prepared paint. Admixture with other pigments prevents this hardening for a long period. This is another pigment the inhibitive power of which is found to vary, owing to indefinite impurities introduced in its manufacture.

Artificial Iron Oxides. — There are a great number of iron oxide pigments used for the protection of iron and steel, and they vary in their specific gravity as well as composition. There can be obtained iron oxides of over 99 per cent. purity, and these are generally made by the burning of copperas (ferrous sulphate), but the resulting materials are apt to contain traces of sulphuric

acid which have not been thoroughly burned out. Oxides made by the above process should be carefully tested previous to use on iron or steel.

Venetian Reds. — The so-called Venetian reds are made by the calcination of mixtures of copperas and lime, the interaction taking place forming ferric oxide and calcium sulphate. The percentage of iron in these Venetian reds varies from 15 to 45 per cent. Because of the soluble nature of the calcium sulphate in this pigment, when not dead burnt, and the ease with which it is ionized in the presence of water, it is considered as a dangerous material to use upon iron or steel. Some Venetian reds are made by mixing iron oxides with gypsum and calcium carbonate. These are considered safer pigments to use, being free from acid, especially when the latter pigment is present.

Metallic Brown. — There are many other oxide of iron ores which are used in the making of paints, and one very important ore is called Prince mineral, or Prince metallic brown. This ore is mined largely in Pennsylvania, and is found as a natural hydrated iron oxide and also as a carbonate (siderite). It is roasted for several hours at a cherry red heat, the hydrated oxide or carbonate being changed to the sesquioxide. It is then ground and made ready for shipment. This pigment contains a considerable quantity of silica and alumina. It has been used both on wood and steel with considerable success for many years, and is considered as one of the standard pigments for protective paints.

Indian Red. — Natural hematite ores and Persian Gulf ores are pigments of great value, and when of the proper shade are termed Indian red. The term Indian red is also applied sometimes to Artificial Iron Oxides made by calcining copperas. These pigments generally run over 95 per cent. oxide of iron, with varying percentages of silica. The shade and tone of Indian red, although varying in many samples, is distinctively more pleasing than many of the brown oxides. The natural iron oxides, made from hematite ores, some of which are termed bright red oxide and Indian red, have a gravity of 3.5 to 5.2 and grind in about 20 to 25 per cent. of oil, while the Venetian red and Prince's metallic brown have a gravity of 3.1 and grind in approximately 25 per cent of oil. The natural iron oxides make valuable body pigments for inhibitive paints.

Ochre, Sienna, and Umber. — There are several other iron oxide pigments, such as ochre, sienna, and umber, the ochre being

a hydrated ferric oxide admixed with clay. The umber is similar in composition to the sienna (consisting of iron and aluminum silicate with varying percentages of manganic oxide which gives it the brown color), but containing a much higher percentage of manganic oxide. These pigments vary in gravity from 3 to 3.5 and they grind in from 35 to 50 per cent. of oil, according to their chemical composition. These pigments are seldom used alone in paints for iron and steel.

Graphitic Pigments. — There are two forms of graphite: the natural, and the artificial. The natural has a gravity of about 2.6, and the artificial of about 2.2. Both varieties grind in approximately the same amount of oil, namely 45 per cent. The natural product is an allotropic form of carbon found in many localities, and contains varying percentages of carbon admixed with silica, and sometimes oxide of iron. The artificial or Acheson graphite contains about 90 per cent. carbon. Burning of this latter variety gives an ash consisting of carbide of silicon, with a very small percentage of silica, iron, and alumina.

Both pigments have been used to a great extent for painting steel and iron, but inasmuch as they have a very excessive spreading rate, a very thin film is produced, which sometimes suffers early decay. Graphite paints are therefore generally mixed with heavier pigments, such as red lead, or sublimed blue lead, producing superior paints. Graphites are not considered good inhibitors by the authors on account of the ease with which they conduct electric currents and thus excite corrosion. The pigment itself is very inert, and has practically no action upon the oil in which it is ground, except to retard drying. It is a very unctuous or greasy pigment and unless reinforced with pigments that have more tooth, it slides under the brush and the particles tend to segregate.

Bone Black. — Bone black is a pigment made from ground bones burned in highly heated iron retorts for several hours. This pigment sometimes contains traces of organic matter and oil which retard its drying. In composition, it runs about 85 per cent. calcium phosphate and 15 per cent. of carbon. Its gravity is 2.68, and it grinds in 50 per cent. of oil to a stiff paste. The authors consider it generally an excellent inhibitor, and it has been used in certain inhibitive paints where dark colors are demanded, to replace carbon black and lampblack.

Lampblack. — Lampblack is a very pure form of carbon, often being over 99 per cent. pure. This pigment is made from the combustion of oils, and is very uniform in its composition. It is extremely permanent and has wonderful tinting strength. It has a gravity of 1.82 and grinds in 75 per cent. of oil. It is an extremely slow drying pigment. It possesses great tinctorial values and is used in large quantities for the tinting of paints. In the authors' opinion, it is not safe to use as a contact coat on iron surfaces, as, like the graphites, it is a good conductor of electricity and therefore acts the part of a stimulator. As a top coating it possesses distinct merit, because of its resistivity to water and its action in preventing early decay of the oil with which it is used.

Carbon Black. — Carbon black is made from the combustion of natural gas, and contains approximately 99 per cent. pure carbon. It has a specific gravity of 1.85 and grinds in 84 per cent. of oil. It has been largely used in admixture with white lead for paints to be used upon steel and iron, but recent investigations have proven that it is a stimulative compound and is dangerous to use as a prime coating material. It may be used with perfect safety as an excluder, when an inhibitive pigment is used for the under coating.

Vine Black and Willow Charcoal. — These pigments are made from the charring of certain grades of wood, and may contain slight traces of alkali which probably account for the excellent inhibitive values which they seem to show. They have a specific gravity of about 1.4 and grind in about 33 per cent. of oil.

Mineral Black Pigments. — Mineral black is a pigment made by grinding an especially black form of slate. Although this pigment does not possess very much tinting value, it has proven of considerable merit as an inert pigment for addition to certain paints. The so-called Keystone filler is made from a bituminous schist ore and forms a dark-colored pigment containing over 50 per cent. of silica, the balance being alumina and carbon, with small quantities of calcium carbonate and iron compounds. This pigment is used extensively as a filler for steel and iron surfaces, especially for machinery.

Orange Chrome Yellow. — Orange chrome yellow is a pigment used largely for tinting purposes and is made from the nitrate or acetate of lead, chromate of soda, and alkali. It is really a

mixture of the neutral chromate of lead and the basic chromate of lead. It is liable to contain small quantities of chromate of soda, basic nitrate or basic acetate of lead, and sulphate of soda. It has a specific gravity of 6.9 and grinds in 20 per cent. of oil. It has good inhibitive values when the impurities are not acid in nature.

Medium Chrome Yellow. — Medium chrome yellow is a pure neutral chromate of lead made from either the nitrate or acetate of lead, and chromate of soda. It has a gravity of 5.8 and grinds in 30 per cent. of oil. It is used in large quantity as a tinting material, its strength depending largely upon the method of manufacture. Like all precipitated pigments, the yellow is likely to carry down small quantities of impurity from the mother liquor. While theoretically an inhibitor, this pigment has not given a very good account of itself on test.

American Vermilion. — American Vermilion is made by boiling white lead and chromate of soda, and adding small quantities of sulphuric acid in order to brighten the shade. A basic chromate of lead is thus formed. This pigment sometimes contains free chromates which account for its excellent inhibitive value. It contains 98 per cent. of lead compounds, and has a specific gravity of 6.8. It grinds in 16 per cent. of oil. It could probably be improved as an inhibitor, if the acid treatment for brightening was omitted.

Lemon Chrome Yellow. — Lemon chrome yellow is manufactured from the acetate or nitrate of lead, bichromate of soda, and sulphuric acid, or a salt of this acid, and is really a mixture of sulphate of lead and chromate of lead. It sometimes contains traces of acetate of soda. It may also contain up to 60 per cent. of lead sulphate. It has a gravity of 6.2 and grinds in 20 per cent. of oil. It is not a good inhibitive, for the reasons given in the description of medium chrome yellow.

Barium Chromate. — Barium chromate is a pale yellow pigment in color, made from barium chloride and chromate of soda. It sometimes contains traces of barium chloride. Like many other precipitated, very slightly soluble chromates, its inhibitive value is not high.

Zinc Chromate. — Zinc chromate is a beautiful yellow pigment manufactured from zinc oxide, sulphuric acid, and bichromate of potash, or zinc salts and bichromate of potash. It has a fairly

high solubility and always contains some impurities. It generally contains free chromates and uncombined zinc oxide. This pigment has a specific gravity of 3.5 and grinds in 25 per cent. of oil. Like the rest of the chromate pigments, it is a very slow drying material, often requiring over a week to set up, unless considerable drier is added. In spite of the impurities which it carries, it has shown itself to be the most inhibitive pigment known and has demonstrated its value in even small percentage in paints for iron and steel. It dries to a hard adherent film that tends to protect metal from corrosion. The authors recommend at least a 2 per cent. addition of zinc chromate to all inhibitive contact coats for iron and steel surfaces.

Zinc-and-Barium Chromate.—Zinc-and-barium chromate is made by precipitation of a solution of zinc and barium chlorides, with chromate of soda. It is a pigment less soluble than zinc chromate, and has proven very efficient as an inhibitive compound.

Chrome Green (Blue Tone).—Chrome green (blue tone) is made from nitrate of lead, bichromate of soda, and oil of vitriol, precipitated on white lead and Chinese blue. The resultant product contains chromate of lead, sulphate of lead, Chinese blue, and white lead. It sometimes contains traces of nitrate of lead and nitrate of soda. It has a gravity of 4.4 and grinds in 25 per cent. of oil. On account of the contained impurities and the comparatively low solubility of this chrome pigment, it does not appear high in the inhibitive class.

Chrome Green (Yellow Tone).—Chrome green (yellow tone) is made from nitrate of lead, Chinese blue, and bichromate of soda. It is liable to contain small traces of lead salts. It has a gravity of 4 and grinds in 22 per cent. of oil.

Chrome Green (Oxide).—Pure oxide of chromium is produced in the wet process by precipitation of reduced chromium salts with alkalis, or, by Guignet's process, by fusion of bichromate of potash with borax, subsequently washing the green powder that is formed, to remove the potassium borate or other soluble salts. It is a very valuable, permanent green, possessing unequalled permanence. It is therefore used for signal and semaphore work on railroads. It possesses good body and covering capacity, and it is inhibitive rather than stimulative. It is, however, rather high in cost.

Prussian Blue.—Prussian blue is a ferri-ferrocyanide of iron

made from prussiate of potash and copperas, by interaction of their solutions, the precipitate formed being subsequently oxidized. This pigment has a gravity of 1.9 and grinds in about 55 per cent. of oil. Like all precipitated pigments, the Prussian blues should be tested for inhibitive value, before their selection. Prussian blue has a marked action in preserving the oil with which it is used, from early decay. It presents a very glossy surface even after long exposure.

Ultramarine Blue. — Ultramarine blue is a very bright blue pigment made from silica, china clay, soda ash, and sulphur, chemically combined by burning in pots and furnaces. The resulting product is ground and bolted. It has a specific gravity of 2.4 and grinds in 30 per cent. of oil. It is not considered a good inhibitive on account of its sulphur content.

Naples yellow, cadmium yellow, verdigris, cobalt, and Brunswick greens and blues, Vandyke brown, and the various alizarin lakes and coal tar colors are seldom used in paints for iron and steel. No description therefore is given of these pigments.

CHAPTER XII

THE PROPERTIES OF PAINT VEHICLES

Linseed Oil. — Linseed oil is the only vegetable oil possessing the necessary drying power and other properties that is produced to-day in sufficiently large commercial quantities to meet the demands of the paint and varnish manufacturer. Attempts have been made to introduce other vegetable oils such as China wood oil, soya bean oil, etc., but their use has been limited by their scarcity or on account of peculiar characteristics which render them unsuited for general purposes.

Linseed oil is produced by crushing and grinding flax seed in specially constructed mills, either of the plate or screw type, the oil being forced out, leaving a residuum of oil cake or flax meal which is used for cattle food. The use of heat in conjunction with the crushing of the oil secures a better yield, and causes the oil to assume a golden yellow color; the color of cold pressed oil is considerably lighter.

Another process utilizes the solvent power of naphtha upon linseed oil. After the crushed seed has been well extracted, the naphtha is distilled from the mixture, leaving the linseed oil. The naphtha is recovered by condensation and used over again for the same purpose.

The flax plant is grown in Russia, India, North America, and Argentine, the latter country producing the largest quantity and representing an average output of over 100,000,000 gallons per year, while the amount of seed produced in the United States gives a yearly production of over 60,000,000 gallons of oil. Minnesota, North and South Dakota, are the states in which most of the seed produced in this country is grown.

The best method of bleaching linseed oil is by proper ageing and exposure to sunlight. Unfortunately this method cannot always be resorted to. Several methods are in use, such as blowing with steam or air, the acid treatment, the use of artificial oxidizing agents, etc. Linseed oil that is treated with sulphuric

acid must be carefully tested before using in paint intended for iron and steel. Blown linseed oil must also be guarded against, as it is rather viscous and is very apt to cause curdling of paint. Mechanical processes of producing pure oil, such as rapid cooling after the oil has been subjected to heat, throws out a large percentage of foots and other objectionable materials. Oil produced in this manner is generally of good quality.

Linseed oil is a triglyceride of oleic, linoleic, isolinoleic, and other organic acids. It is a saponifiable oil, and when treated with alkali the acid part of the oil forms salts or soaps, liberating free glycerine.

When spread upon glass in a thin film, raw linseed oil dries in about four days. This drying takes place by progressive oxidation, the oil increasing in weight by the addition of oxygen, without any appreciable decomposition or elimination of its own constituents. The initial oxidation is slow, but the formation of peroxides causes the oxidation to proceed very rapidly. The use of certain non-drying pigments with linseed oil, such as carbon black or lampblack, retards this drying for several days, while the use of other pigments, such as zinc oxide, red lead, litharge, and white lead, increases the drying action of the oil. It is therefore apparent that in the manufacture of paint, the amount of drier to use must depend on the composition of the paint.

Chemical Characteristics of Linseed Oil. — Linseed oil possesses certain characteristics which are utilized by the chemist to determine its purity. Among the most important of these characteristics are the saponification value, the iodine number, the acid value, and the specific gravity. If the oil is suspected of adulteration with mineral oils, treatment with caustic alkali will at once yield evidence whether such is the case. Linseed oil is almost totally saponifiable, and in the presence of alkali forms a soap, while mineral oils are unsaponifiable and are unacted upon by the alkali. The saponification value of linseed oil is approximately 192, other saponifiable oils varying to greater or lesser extent in this value.

Linseed oil always contains traces of free vegetable acid uncombined with glycerine, the amount generally averaging not over one per cent. The presence of a high percentage of free acid in an oil would indicate the addition of rosin or rosin oil, as the latter oils both possess a very high percentage of free uncom-

bined acids. Excessive free acid in linseed oil is often the cause of the gelatinization or thickening of paints containing lead and zinc, this action being due to the formation of soaps with the pigments of basic nature, in the paint.

All vegetable oils differ in the amount of iodine which they are capable of absorbing; this iodine absorption property being in direct relation to the ability of the oil to absorb oxygen. The iodine absorption test is very valuable in the determination of the purity of an oil.

The specific gravity of an oil is also a good criterion of its purity, and often will readily indicate whether the oil has been adulterated with lighter or heavier mineral oils. The presence of petroleum products may be noted by their odor, and this latter test is also used when linseed oil is suspected of containing fish oils, the characteristic fishy odor being developed when the oil is slightly heated.

The Maumené test, or rise in temperature, when oil is treated with sulphuric acid, has been of value in detecting the presence of petroleum spirits. The flash test is also in vogue for this purpose. The refractive index and oxygen absorption test are also used in the determination of the purity of linseed oil.

When a sample of raw linseed oil is spread upon glass, and the drying observed, the condition of the film is sometimes indicative of the presence of mineral or fish oils, cloudiness of film or excessive tackiness indicating their presence or the presence of some semi-drying oil such as cottonseed oil.

The following characteristics of linseed oil gives the average results of several analyses of the pure oil:

Specific Gravity at 15.5° C.....	.932 to .935
Acid Number.....	5 to 7
Saponification Value.....	187 to 192
Unsaponifiable Matter.....	.8 to 1.5%
*Iodine Number.....	180 to 190
*(May sometimes be as low as 160.)	

During the drying of linseed oil, certain changes in its molecular structure, due to the absorption of oxygen, takes place, and the film may become more or less porous, allowing the admission of moisture which would cause the corrosion of underlying iron. Toch¹

¹M. Toch. The Chemistry and Technology of Mixed Paints, p. 88. D. Van Nostrand Co., New York, 1907.

has stated that moisture goes through a linseed oil film by forming a semi-solid solution with the oil, as microscopic examination of films fails to reveal the existence of pores. While Toch's statement is undoubtedly true, it does not argue that a form of porosity does not exist. Semi-solid solution demands intra-molecular spaces that can be occupied by water molecules. Whether we call these spaces pores or something else, they must exist, even though the microscope is incapable of resolving them.

The use of linseed oil as a shop coating is not good practice and has probably been the cause of much damage. Repainting over such a coating, with good results, is almost an impossibility. When a linseed oil film on iron is abraded at any point on the surface, corrosion will proceed rapidly. As Walker¹ has shown, the hydrogen which is evolved during the initial start of corrosion would, under ordinary conditions, form an electrolytic double layer, to some extent preventing further corrosion. The linseed oil, being an unsaturated hydrocarbon, acts the part of a depolarizer and therefore the action is accelerated. Inhibitive pigments in the oil, however, retard this action and overcome the stimulating effect of the oil film.

The presence of mucilaginous and albuminous matter and certain solid fats causes the "foots" or cloudy sedimentation in linseed oil. A high percentage of foots should be avoided, because of the high acid number and destructive effect on the dried film of linseed oil.

Boiled Oil. — Boiled linseed oil is made by adding lead or manganese salts or oxides to raw linseed oil, heated to 350° F. Solution takes place, with the production of an oil which has very rapid drying power. When spread in a thin film on glass, eight hours is sufficient to set the oil up very firmly without tackiness. This oil is extremely valuable in the manufacture of paints for iron and steel.

Other methods of making boiled oil produce inferior products; the so-called "bung hole" oil, in which a liquid drier, or thick mixtures of boiled oil containing salts and oxides, is added to cold raw oil in the barrel, is quite common. This method is to be deplored, as it produces an inferior grade of oil.

Chinese Wood Oil. — Chinese wood oil is obtained from the

¹ Wm. H. Walker. The Function of Oxygen in the Corrosion of Metals. Trans. Amer. Electrochem. Soc., Vol. XIV, 1908.

nuts and seeds of the Chinese tung tree, and imported in large quantities for use in the manufacture of special varnishes and paints. The raw oil is unsatisfactory for use, drying white and unelastic, but when heated at certain temperatures, less than 250° F., and treated with salts or oxides, then thinned with oil and benzine, an excellent product is obtained. The treated oil dries rapidly, with a high gloss and heavy body, producing a hard, elastic film which seems to be relatively moisture proof. On account of these properties, it is largely used in the manufacture of floor paints and enamels, but has not as yet received any special application in the manufacture of paints for iron or steel. Films, however, made with this oil seem to possess excellent excluding and moisture resisting properties.

Toch¹ says: "By the use of China wood oil, paints are made which dry in damp atmospheres. The advantage which the Chinese and Japanese have had over the Europeans on this subject has been recognized for a long time. It is now known to have been due to their knowledge of the proper manipulation of China wood oil. For the making of marine paints and waterproof paints China wood oil is indispensable." It is probable that this material will be more extensively used in the future for making up protective paints for iron.

Soya Bean Oil. — This oil is produced from the soya bean which grows in Manchuria,² the product being used largely in the manufacture of soaps. It possesses such close resemblance to linseed oil that it is difficult for the analyst to determine its presence. Experiments are being made to utilize it in place of linseed oil, but only a few hundred gallons have been received in this country up to the present time. Soya has a slightly darker color than linseed oil. The following chemical characteristics will show how closely it resembles the latter:

Specific Gravity924
Saponification Value.....	192
Iodine Value	122-130

It dries rather slowly, with the production of an elastic film.

¹ M. Toch. Chemistry and Technology of Mixed Paints. D. Van Nostrand Co., New York, 1907.

² Attention is called to the fact that the Soya bean grows well in many parts of the United States although it has not been used as a source of paint oil.

Special treatment may render this oil of great value in the manufacture of protective paints.

The Use of Driers.—The necessity of having the oil dry gradually, but still with enough speed to prevent undue tackiness with the resulting dust-catching properties, demands the use of a drier that will cause oxidation to proceed uniformly and with the proper rate of speed. The too rapid oxidation of linseed oil, with the formation of linoxyn, is the cause of the non-elasticity and brittleness of some paints that have been recently used. This effect is more noticeable in paints containing japan driers than in those containing oil driers, the latter being the safest of the two varieties to use. Japan driers are manufactured by fusing resins with salts and oxides of zinc, lead, manganese, and other metals, reducing the mass at the proper time with turpentine or light mineral oils. The drying action of japan driers is very rapid. The oil driers are made by heating linseed oil with salts or oxides of metals, at a high temperature, subsequently thinning down with more oil and volatile diluent, preferably turpentine.

Oxides of lead and manganese are the most widely used chemicals for the making of driers. Manganese starts the drying action and causes rapid surface drying. The lead drier causes the oxidation to proceed throughout the film and should generally be in the larger proportion. Red lead and litharge are also used, but red lead causes a brittleness of paint films, while litharge gives a paint film very elastic properties.

Turpentine.—This remarkable and highly prized paint diluent is distilled from the sap of the pine tree. The largest quantity is being produced in the pine forests of Georgia and South Carolina. In its pure form it is a water white liquid, easily recognizable by its distinctive odor. When added to paint, it prevents thickening of the paint and causes the paint to work very freely under the brush, increasing its spreading properties. It is largely used for flattening purposes, and it evaporates slowly but completely, causing more rapid oxidation of the oil in which it is used. It evaporates on paper without a stain, and this test, accompanied by tests for its specific gravity, polymerization value, and flash point, makes its adulteration easily detected.

Sulphuric acid, when mixed with turpentine, results in the formation of a brownish colored, thick liquid, the turpentine

being polymerized with the acid to other compounds. The presence of mineral oils which are unacted upon by sulphuric acid, is readily shown by this test, and they separate and float upon the top of the polymerized liquid.

A pure turpentine will show the following characteristics, within very close limits:

Specific Gravity.....	.86 to .87
Boiling Point.....	156° C.
95% will distil between 150 and 165.	
Polymerization test—less than 5% should be unacted upon by sulphuric acid.	
Spot test—should completely dry on filter paper without stain, and without affecting the water-absorptive properties of the paper.	
Flash point—should not be under 40° C.	

Wood turpentine is made by distilling pine debris and logs. This process produces a liquid having an odor very much more penetrating than pure gum spirits, and its effect upon workmen is sometimes serious. Proper refining may remove pyroligneous and formic acids, pyridine bases, and creosote, which it contains in small quantities, producing a product that is almost identical in painting values with the pure gum spirits. It has been found, however, that the most highly refined wood spirits contains a slight difference in the relative percentage of pinene, and turpene, to that contained in pure gum spirits.

Paraffine Spirits.—These are produced to-day by the refining of petroleum and asphaltum products. In the refining of petroleum, several light oils, such as benzine and naphtha, are produced and are largely used by the painter as cheap diluents. They evaporate very rapidly, but their excessive use should be condemned. The very low flash point of these products make them somewhat dangerous. Several higher boiling point oils are produced in the distillation of petroleum and asphaltum compounds. In their flash point and boiling point they resemble pure turpentine, and they answer to the spot test satisfactorily. They possess the same flowing and flattening properties as pure turpentine, and are being used in considerable quantities as a substitute for this material.

Benzol.—This product is obtained by the distillation of coal tar, and is a chemical compound corresponding to the symbol C_6H_6 .

It is a water-white liquid of excellent penetrative and solvent properties. It has been found valuable as a diluent for coal tar and asphaltum paints, and is largely used in the manufacture of paint and varnish removers.

Lacquers and their Application.—By the term “lacquer” is meant the pale varnishes so largely used in the protection of brass, copper, and silver ornamental work. Lacquers have been used to some extent in the protection of steel and iron, and a short outline of their manufacture will not be out of place.

There are three distinct varieties of lacquers, known as gum lacquer, cotton lacquer, and the combination lacquer. Gum lacquers are produced by dissolving broken gums, such as kauri, sandarac, and shellac, in cold grain alcohol, fusel oil, acetone, and other solvents. They may be colored with various coal tar dyes. They are applied with a brush, and rapidly dry to a very transparent film with a high gloss. Materials so lacquered are often baked to insure a harder film.

The most widely used lacquer is cotton lacquer. This lacquer is made by dissolving soluble nitrated cotton in amyl acetate. The cotton is manufactured by immersing perfectly clean absorbent cotton in a mixture of nitric and sulphuric acid. The cotton used may be either the long, staple variety, or the short-fibered, pulp variety; the former producing the best and most elastic lacquer. During immersion in the acid, the cotton becomes nitrated, taking up two molecules of nitric acid. The strength of the acid, and temperature at which nitration takes place, are extremely important, as several varieties may be produced, all of which have different solvent values. The cotton after nitration is removed from the acid and thoroughly washed and neutralized. It is then dried and treated with solvent. Amyl acetate, acetone, wood, and grain alcohol are used as solvents, but only the first-named solvent produces a transparent film. Articles to be coated with cotton lacquer must be dipped, as brushing causes streaking.

Combination lacquer is made by combining a gum lacquer and a cotton lacquer, the solvents of which have been properly adjusted to prevent settling out or curdling of either constituent. Combination lacquers are very serviceable and of extreme value for protecting metal ornaments.

One of the authors has used a chromated lacquer which has

given good results in protecting iron articles on a small scale. Gum shellac is dissolved in grain alcohol and the insoluble wax filtered out. Chromic acid is then introduced into the lacquer by adding tiny pinches at a time until saturation has taken place. If the chromic acid is added carelessly or in large increments, violent oxidation will take place, and the lacquer may take fire. For this reason it is well to have the vessel containing the solution surrounded by ice water while the lacquer is being chromated.

Perry has developed a chrome resinate which gives promise of proving itself a valuable constituent of inhibitive vehicles. This compound is soluble either in benzol or linseed oil, and when used in very small percentage may be of value as an additional fortifier against corrosion.

Varnishes. — Varnishes will not be discussed here, as they are used almost entirely for interior decorative purposes. It has been demonstrated, however, that a percentage of high-grade varnish in a paint renders that paint a better excluder of moisture. If the varnish be of a nature that will stand exposure, its use is desirable, in some instances.

APPENDIX A

PRESENTING A DISCUSSION BEFORE THE AMERICAN INSTITUTE OF MINING ENGINEERS ON THE CORROSION OF WATER JACKETS OF COPPER BLAST FURNACES.

*The Corrosion of Water Jackets of Copper Blast Furnaces.*¹ — During the two years in which the new reduction-works of the Copper Queen Consolidated Mining Company have been in operation at Douglas, Arizona, there has developed a remarkable condition in regard to the corrosive action of the water used to cool the jackets of the blast furnaces.

Were it not for the many contradictory features, it might pass as one of the unavoidable troubles due to the composition of the water. This water, obtained from wells 600 ft. deep, is also used in the steam boilers, and its composition, as shown by the following analysis, does not indicate the presence of any ingredient which would explain the corrosion:

	Grains per U. S. Gallon.
Silica	0.861
Iron oxide and alumina	0.223
Calcium carbonate	0.261
Calcium sulphate
Magnesium carbonate
Sodium and potassium sulphates	14.850
Sodium and potassium chlorides	9.732
Sodium and potassium carbonate.....	6.482
	<hr/> 32.409

The jackets are made of inner plates 0.5 in. thick, and an outer plate $\frac{3}{8}$ in. thick, with $\frac{3}{8}$ in. stiffeners between the inner and outer plates. In from ten to twelve months the inner plates have been reduced by corrosion to a thickness of from $\frac{1}{8}$ to $\frac{1}{16}$ in., while the outer plate in the same time is reduced by less than $\frac{1}{16}$ in., and the stiffeners show very little corrosion. The plates are

¹ Transactions of the American Institute of Mining Engineers. By George B. Lee, Douglas, Arizona. (Toronto Meeting, July, 1907.)

pitted and eaten away in some places more than in others. There is practically no scale found on the jackets, but when cleaned considerable iron oxide is found in the bottoms.

With an action so marked, serious trouble would be expected in the boilers, but, on the contrary, a recent inspection by a boiler insurance company gave an almost perfect report on the large boiler plant, which consists of eight 500-h.p. Sterling boilers. There was no pitting in the tubes. The inspector's attention was particularly called to the pitting of the jackets. The cast-iron impellers of rotary pumps that pump to the cooling tower from the hot-well are pitted in spots quite as deeply as the jackets. A sheet-iron pipe 0.25 in. thick, that has carried all the hot water for the jackets of eight furnaces, has never leaked. Some wrought-iron pipes, handling water at a temperature of from 65° to 80° F., have been almost destroyed by pitting, while others in the same line have not shown a leak.

These notes are offered in the hope that some member of the Institute may have met this problem before, and can throw light on this interesting subject.

DISCUSSION

William Kent, Syracuse, N. Y. (communication to the Secretary¹): The analysis of the water shows it to be somewhat unusual; it is rather high in sodium and potassium sulphates and chlorides, 24.58 grains per gal., and very low in calcium carbonate, 0.261 grain per gal. There are three theories which may account for the corrosion:

1. *Air Bubbles Lodging on the Iron.* — It is well known that even pure water, such as the water of condensation from steam-heating systems, is an active agent in causing the pitting of the nipples used for connecting cast-iron radiators and the iron or steel return water-pipes, and the presence of air in the water is supposed to be the real cause of corrosion.

2. *Electrolytic Action.* — The water containing sulphates and chlorides may act as an electrolyte, and different portions of the steel plate, having slight variations in chemical composition, may act as two different metals or electrodes.²

¹ Received July 17, 1907.

² See Dr. Cushman's paper on Corrosion, read at the 1907 meeting of the American Society for Testing Materials.

3. *Chemical Action.*—At certain temperatures potassium sulphate may attack iron, forming iron and potassium sulphate.

Possibly all three of these actions may take place at the same time.

The remedy indicated is the addition of a little milk of lime to the water. This will neutralize any acid reaction of the potassium sulphate, and form a precipitate of calcium sulphate, which will make a protective coating on the iron and prevent all three of the actions above described.

James Douglas, New York, N. Y. (communication to the Secretary ¹): The following extracts from correspondence with Mr. Lee give some additional particulars concerning the corrosion of the jackets:

DOUGLAS, ARIZ., June 12, 1906.

We have just taken out from one of our new furnaces a jacket, which has been in use five months. I find the same trouble as before, the inner sheet is very badly pitted. The outer sheet and the angles that space the inner and outer sheets do not appear to be attacked.

In connection with this, I wish to call attention to the fact that our boilers, which have been in use now for two years, have just been inspected by the insurance company and have received an almost perfect clearance. Apparently the corrosion is due to some peculiar condition that exists with the fire on one side and water on the other; and also that there is a difference between this condition and that obtaining in the boilers. The steel plate on the outside, which is much thinner to start with, and which is air-cooled on one side, with hot water on the other, far outlasts the thicker inner sheet, and the T-irons, or angles, which are immersed in the water between the two sheets, seem to be very little attacked.

In connection with this peculiar action, I would call attention to the impellers in the rotary pumps which circulate the water for the condensers in the power plant. These are made of cast-iron; and we find that at certain points they are very badly pitted, being eaten away to a depth of a quarter of an inch for a space of one or two inches in area; and right next to this there will be spaces that are apparently not attacked at all. We have had

¹ Received September 28, 1907.

whole lengths of pipe, leading from the supply tanks to the powerhouse, which were perforated, and lengths next to them apparently very little attacked. The surface of the jacket seems to be more uniformly attacked, but even on this there are smooth spots that have apparently resisted this action.

You will see from the above that materials as different as flange steel and cast iron are both attacked by the water; that steel exposed to very hot water, such as exists in the boilers, is apparently not attacked; that pipes handling water not over 75° F. are attacked; that pumps handling water both cold and moderately heated are attacked; and that steel surfaces heated on one side and with water on the opposite side of, say, 140 to 150° F., are badly attacked, while plates cooled on one side by the air and exposed to the same water are very little attacked.

I suggested that samples of the inner shell and a stay-bolt be sent for inspection by the members of the Institute, and that the temperature of the water in contact with the inner and the outer shell be taken. To this request the following reply, dated December 11, 1906, was made:

Complying with your request; I am sending to-day, by express, a stay-bolt and piece of metal from a water jacket. The temperatures which you suggested taking of the jacket water near the inner sheet and near the outer sheet have been taken repeatedly, and I enclose a statement showing the range of temperature. You will note that, as the temperature increases, the variation also increases. We have just now a report from the inspector of the Hartford Boiler Insurance Company, in which we are given an absolutely clear bill on the entire battery of boilers, six of which have been in use 3½ years.

I believe I told you on your last trip here that we are now making experiments by feeding oil into the water as it goes to the jackets, with the hope of coating the inside of the jacket with a film of oil, and possibly preventing the corrosive action of the water.

TEMPERATURE OF WATER IN JACKETS NEAR THE INNER OR FIRE SIDE AND
OUTER OR AIR SIDE.

Outside Degrees F.	Inside Degrees F.	Outside Degrees F.	Inside Degrees F.
97	106	104	115
98	107	106	115
98	108	108	118
102	112	116	130

In answer to a request as to the effect of this oil, Mr. Lee wrote August 28, 1907, as follows:

I am in receipt of your wire of the 22d in regard to corrosion of water jackets. Apparently the use of oil has been of some benefit in reducing this corrosion, as the amount of jackets renewed seems to be little more than it was, though the number of jackets in use is considerably larger. I recently had occasion to examine a jacket which had been taken out, and found a very peculiar condition; namely, there was a place about 6 by 8 in. right in the middle of the place which seemed to be quite smooth and not pitted at all, while all around, it was very badly corroded. This jacket had been in use about a year and a half.

I have received a very interesting letter from Mr. Beardsley, who was formerly with the Mt. Lyell Company in Tasmania, giving me a number of experiences that he had had of corrosion of jackets, and, as far as he was able, the causes. In one instance well-water was substituted for the former supply. The well-water seemed to be highly charged with gas, and they experience great difficulty from the jackets burning. This he attributed to the formation of gas-bubbles on the fire-sheet. By mixing the city water and this water the trouble was very much reduced, and a return to the city water stopped it entirely. This, of course, is quite a different experience of ours, which is not one of burning, but one of interior corrosion.

The following letter, dated London, September 17, 1907, is from George M. Douglas, a member of our staff, who was an engineer for some time on the White Star and other steamship lines: On reading the correspondence you have received from Mr. Lee at Douglas regarding the corrosion of the inner plates of

the furnace-jackets, I suggest that this might be caused by some electrolytic action. This same corrosion takes place in the Scotch type of marine boiler, particularly when the water contains a little salt. This boiler is somewhat analogous in form with the jacket, having a hot inner plate, a water space, and relatively cool external shell.

This corrosion is prevented by hanging zinc plates on the stay-rods between the spaces affected. It is also a practice to put zinc plates near the water inlet, so that any free acid in the entering water may combine with the zinc and be neutralized.

Perhaps a similar application of zinc to the jacket shells at Douglas might prove beneficial. I suggest applying it in the following manner: The zinc plates should be about $\frac{3}{4}$ in. thick, and about 8 in. wide, and 16 in. long. Some authorities object to the application of zinc direct to the iron, though it is customary to do so in British engineering practice.

A suitable means would be to have brackets made of copper strips, $\frac{3}{8}$ in. by 1.5 in., placed about a foot above the bottom of the jacket on the inner shell, into which brackets the plate could be inserted from the top.¹ I also suggest that a plate be put where the water jacket enters. Two plates of the size mentioned on each side and one on each end of jacket (should there be any corrosion there) is enough. I do not know what the size of the furnaces is. But the relative proportion of zinc surface to iron surface should be about one to ten. A good contact should be insured between the zinc and the copper and iron, or, if copper is not used, between the zinc and iron.

It is not enough merely to place the plates in the water space; they should be well fastened to the jacket.

Under the same date, Mr. Douglas, in response to an inquiry from me, made, in substance, the following statement, which, although not directly pertinent to the present discussion, may be valuable as a contribution to the general question of the corrosion of steel and iron:

With regard to the corrosion of stern-posts and plates in the vicinity of propellers on ships, I should say that this action seems to be well understood as due to the fact that the propeller-blades

¹ This suggestion is not a good one, as the zinc would be destroyed in protecting the copper instead of the iron. A. S. C.

etc., on one hand, and the stern-posts and plates, on the other hand, are of different material, so that a galvanic action is set up, the salt water acting as an electrolyte. If all these parts were of exactly the same material, no corrosion would take place; but this is not the case in practice. The stern tube is usually of bronze, and the propeller of bronze and steel, with blades of manganese bronze. An interesting case is on record, of a vessel on which iron propeller blades were replaced by blades of bronze. Immediately upon this change, the corrosion of the stern post and surrounding plates became so great they had to be renewed after only one voyage to the Cape. They were afterwards protected by zinc sheathing; and it is now the custom to protect such parts by sheathing of zinc or some metal of similar electro-chemical character.

Though these facts are interesting, I fear they will not help you much in dealing with your jackets, since the conditions of your problem are by no means the same as those of the marine practice above stated, in which both the origin and the remedy of the trouble seem to be clearly established.

With regard to the general question of the corrosion of steel or iron plates, however, I may call your attention to one point which may be worthy of consideration — namely, the electro-chemical relations between metals and their oxides. According to a leading author,¹ “every metal is electro-positive to its own oxide.” When steel or wrought-iron, with oxide scale upon it, is placed in an oxidizing liquid, the conditions of active corrosion are complete; and even without a specially oxidizing medium, it is asserted that a galvanic action may be set up in the presence of air and moisture between the metal and its scale. It is therefore regarded as very important that no “black oxide” should be left on the plate; for, though in itself it tends to protect the surface (the black or magnetic oxide of iron resisting ordinary oxidizing agents), yet if, in finishing, handling, or subsequently using the plates, portions of it should be knocked off, the remaining portions contribute to the corrosion of the exposed metal.

In 1879, Sir Nathan Burnaby declared, as the result of his

¹ *Metallic Structures: Corrosion and Fouling, and their Prevention*, by John Newman, p. 36. London: Spon & Chamberlain (1896). See also *Rustless Coatings, Corrosion and Electrolysis of Iron and Steel*, by M. P. Wood. London: Chapman & Hall (1904).

observation, that when mill-scale was left upon plates and angles used in ships, its effect upon neighboring surfaces of bare metal was as strong and continuous as that of copper.

In 1882, Mr. Farquharson conducted for the British Admiralty, at different naval stations, exhaustive experiments as to the action of mill-scale on ships' metal exposed to the conditions of marine use, and found: (1) that no "pitting" occurred in mild steel freed from all scale; (2) that the loss of weight by corrosion was practically the same for clean mild steel and clean iron; and (3) that the action of mill-scale in inducing corrosion is considerable and continuous — equal in these respects to that of an equal amount of copper.

The Admiralty practice is to pickle all ships' metal, for the removal of mill-scale. The scale may also be removed by sand-blast, or by means of a gasoline-torch, followed with a scraper and a wire brush. Pickling, however (in dilute sulphuric or hydrochloric acid), is probably more thoroughly effective.

The rivets should be of the same material as the plates. Iron rivets in steel plates might cause trouble.

Hiram W. Hixon, Victoria Mines, Ontario, Can. (communication to the Secretary ¹): I have had difficulties here similar to those encountered at Douglas, and I found the cause to be the carbonic acid given off when the water was warmed. All the water in the streams in this country contains organic matter coming from peat-bogs and muskegs. It is brown in color, and when it strikes the fire-sheets of the jackets the carbonic acid is given off and travels up along these fire-sheets because of the bosh in the furnace. The lower side of the tuyeres was much pitted, and they leaked badly until I had copper tubes put in in place of iron ones.

The inner or fire-sheets were destroyed most rapidly opposite the cold-water inlet, where the greatest amount of carbonic acid was given off. Our boilers are not affected and are perfectly clear of scale. I think the acid is liberated in the feed-water heater, in which there are copper tubes, and after it is in a gaseous condition it does not attack iron, or at least the water is necessary to make it destructive. The pipes leading from the feed-water heater to the boilers are destroyed, but the boilers are not.

¹ Received through Dr. Douglas, Sept. 28, 1907.

The Canadian Copper Company had a purifying plant for the feed-water, and the pipe leading from the purifier to the different boilers went over the boilers, and each lead to the boiler came out of the bottom of the main pipe. Tests made of the water to the different boilers showed that the water to the boilers nearest the purifier was much less acid than the water to the boiler at the end of the feed-pipe. The superintendent spoke to me about it, and I suggested that the acidity of the water was due to carbonic acid dissolved in the water, and that being a gas it had a tendency to enrich the water in the top of the feed-pipe, and, consequently, the water drawn off for the first boiler from the bottom of the main contained less acid than the water which went to the last boiler.

I think the trouble at Douglas is due to the water supply coming from the deep wells containing carbonic acid, and this acid is probably due to the source of the water being something in the nature of a mineral spring, such as Saratoga, Manataw, or Apollinaris. Ordinary chemical tests would fail to detect any mineral acid, and the gas being small in quantity would escape detection.

The remedy for the trouble is to use copper fire-sheets, or to run the water through cooling towers and use it after the carbonic acid has escaped.

C. D. Van Arsdale, New York, N. Y. (communication to the Secretary ¹): There are several explanations which present themselves regarding the corrosion of the water jackets of the Douglas furnaces. The most obvious of these — namely, that the composition of the water is itself directly responsible — may be dismissed as improbable. Analysis of the water shows that it may be called a good boiler-water for this region, since it contains very small amounts of incrusting solids and the non-incrusting solids are not excessive; and this opinion is verified by its causing practically no boiler troubles. Since no corrosion takes place in the boilers, it is evident that the dissolved constituents of the water do not alone afford sufficient explanation.

Granting that the water is itself non-corrosive, there is nothing in the working of the ordinary water jacket to account for the difficulty, otherwise such corrosion would be more or less gener-

¹ Received October 31, 1907.

ally observed in other plants. It would, therefore, seem that the only explanation left is electrolytic action; but it is not evident what is the cause for electrolysis.

It is well known that lack of uniformity in the composition of iron will cause corrosion on account of action due to minute local galvanic couples. If this is the cause, then a suitable remedy would be to hang zinc sheets inside the jackets, as has already been suggested. Another cause of electrolytic corrosion may be stray currents from some source. In the same way much trouble has been experienced from corrosion of gas- and water-mains in cities, due to stray electric currents passing along them. A very small current has been found sufficient to cause a great amount of trouble, but if this should be found to be what is causing the electrolytic action in the jackets, it should be quite simple to put a stop to it.

The different temperatures observed in different parts of the jackets might also be sufficient to cause some corrosion, since electrical currents can be produced in an electrolyte by electrodes of the same metal, portions of which are at different temperatures. This could be obviated by a circulation of water in the jackets sufficiently rapid to do away with any differences of temperature.

The fact that the jackets are much more corroded on the fire side seems to indicate that the electrolytic action is due not to lack of uniformity of the iron, but to one or both of the other causes mentioned.

*The Corrosion of Water Jackets of Copper Blast Furnaces.*¹ — C. D. Demond, Anaconda, Mont. (communication to the Secretary): In order to throw some light on this interesting subject, a series of experiments were made with strips of mild steel, containing about 0.14 per cent. of C and 0.22 per cent. of Mn. These strips were thoroughly cleaned and brightened before use, salts were added to distilled water until it corresponded as nearly as possible to the analysis given by Mr. Lee, and in this water at different temperatures were placed four strips of steel; while four other strips, at corresponding temperatures, were placed in the water used at the Washoe Reduction Works. The latter plant has had no trouble from corrosion of furnace jackets, pipelines or boilers.

¹ (Transactions of the American Institute of Mining Engineers, xxxix, 806-817.) A discussion of the paper of Geo. B. Lee, Trans., xxxviii, 877 to 884 (1908).

The analysis of the water used at the Washoe works is:

	Grains per U. S. Gallon
CaCO ₃	2.92
CaSO ₄	0.76
MgCl ₂	0.64
MgCO ₃	0.58
Al ₂ O ₃	0.12
Fe ₂ O ₃	0.12
SiO ₂	0.58
NaCl	0.35
Organic matter, etc.	1.16
	<hr/> 7.23

This water is neutral to litmus; while the artificial Copper Queen water is very slightly alkaline, which Mr. Lee informs us is also true of the water at Douglas.

Both waters were well aerated by pouring from beaker to beaker, and by blowing in air from the experimenter's lungs. The results of these tests, given in Table I, show that there is no significant difference between the effects of the two waters.

TABLE I.—OXIDATION OF IRON PER SQUARE INCH OF SURFACE* WHEN IMMERSSED IN CERTAIN WATERS.

ARTIFICIAL COPPER QUEEN WATER			
Average Temperatures	First 50 Hours	Second 50 Hours	Total
	<i>Mg.</i>	<i>Mg.</i>	<i>Mg.</i>
70° F.	1.943	1.360	3.303
106	5.322	3.963	9.285
150	5.206	4.701	9.907
185	2.865	1.642	4.507
WASHOE WATER			
70° F.	2.797	1.516	4.313
106	5.178	3.746	8.924
152	6.618	6.422	13.040
188	1.784	0.699	2.483

* These results were obtained by carefully rubbing all the rust from the iron, dissolving it, and determining its quantity by titration.

At two temperatures the strips of steel in the Copper Queen

water showed less rust than those in the Washoe water, while at the other two temperatures they showed more. Another experiment indicated that distilled water would have given about the same results. Hence, the corrosion of the Copper Queen jackets must be due to some other cause than the quality of water. I am informed, however, that the water is raised from artesian wells by means of compressed air, and, after being used in the furnace jackets, is passed over a cooling tower, and later goes to the jackets again. Hence it probably contains an excessive amount of dissolved oxygen. It will be noticed that rusting increased with the temperature, up to 150° F., as is true of chemical actions in general; but at 185° there was decidedly less rust than at 150°, presumably due to the water at the higher temperature being unable to hold enough oxygen in solution to keep up the rate of oxidation.

The small differences of temperature (9° to 14° F.) do not seem sufficient to account for the inner plates rusting more than six times as fast as the outer; but is it not probable that the temperature of the very surface of the inner plates is considerably higher than is shown by inserting a thermometer in the water, and that an unusual amount of dissolved oxygen at this temperature is the cause of the trouble? The jackets would probably suffer much less if the water were discharged as near the boiling point as practicable, and returned directly to the supply tanks; the return pipe should dip well beneath the surface of the water in this tank, since a plunging stream would entrain a fresh quantity of air. This would lessen the amount of dissolved oxygen, and rust cannot form without oxygen. Referring to the first two paragraphs of Mr. Hixon's discussion,¹ it is the gases in solution that are active, not those given off; and the probable reason for his jackets corroding most rapidly opposite the cold-water inlet is that the water at that point still holds the gases in solution. The absence of rust in the Copper Queen boilers, and in those at the Victoria mines, is perhaps due to the elimination of absorbed gases immediately on entering the boilers and before the water can touch the metal. It is certain that the temperature of the water increases very rapidly upon entering the boilers.

We have experimented with several other remedies. The well-known use of zinc is completely effective when the zinc is

¹Trans., xxxviii., 882 (1908).

properly distributed; but this metal corrodes so rapidly that it has to be frequently renewed. Copper, on the other hand, increases the rusting of the steel, these results being due to the electro-chemical relations of the metals.

Knowing that solutions of alkalis and alkaline salts sufficiently strong will prevent rusting, we tried the effect of lime, at approximately the temperature of the water in the Copper Queen jackets. An increase in the quantities of lime added up to 0.1 per cent. gave increased benefit, amounting to practically complete prevention with the Washoe water, and reducing the rust in the artificial Copper Queen water about 60 per cent. The difference was evidently due to the reaction of the lime with the sulphates and carbonates in the latter water. Larger amounts of lime would probably complete the cure, but the precipitate might have to be settled out.

Dr. A. S. Cushman¹ found, in certain experiments, that potash bichromate completely prevented rust when dissolved in water at the rate of 1 lb. or more in 1500 gallons. Our tests indicate that, even in using the water over and over in the jackets, the bichromate would be slowly exhausted, requiring fresh additions at intervals. We have not yet determined what the cost of treatment would be; but the protective effect is very striking.

The elimination of dissolved oxygen from the water is suggested as the practical remedy in this particular case; but we may take occasion here for some further remarks on the general subject of rusting.

The fact that some wrought-iron pipes at Douglas are practically unaffected, while others in the same line, as well as the furnace jackets, are badly corroded, strongly suggests that there is some trouble with the metal itself, and that it is not a question of wrought iron versus steel. Indeed, the most recent and reliable industrial and scientific investigations show that the long-standing controversy as to the relative rust-resisting qualities of wrought iron and steel is largely a beating of the air. The real question seems to be one of care in the processes of production. Cushman² very ingeniously demonstrates that an appar-

¹ Bulletin No. 30, Office of Public Roads, U. S. Department of Agriculture, and Proceedings of the American Society for Testing Materials, Vol. VII, p. 211 (1907).

² *Loc. cit.*

ently homogeneous piece of iron or steel carries a multiplicity of positive and negative poles of an electrolytic system; and the electrolysis between them increases the speed of rusting at the positive pole, while preventing rust at the negative. He suggests that this polarity is due to uneven distribution of certain chemical constituents of the metal. In answer to the fact that frequent investigations have failed to show this uneven distribution, he says¹ that "such extremely small differences in the chemical composition as might easily escape detection in ordinary chemical analysis are still sufficiently large to account for slight differences of electrical potential." He might have added that there may be considerable difference in composition which chemical methods cannot detect, because it is impossible to sample the segregations separately. Frank N. Speller,² on the other hand, thinks that variations of density may sometimes account for the polarity. However, there is no doubt as to the existence of the polarity; and its effect was well shown in one of our test strips, 4 in. long, after an exposure of 50 hours in water. A large part of the surface shows perfectly bright, but other parts are badly rusted. Mr. Lee says "the plates are pitted and eaten away in some places more than in others"; also, that in one case "there was a place about 6 by 8 in. right in the middle of the plate which seemed to be quite smooth and not pitted at all, while all around it was very badly corroded." The greater the difference of potential the greater will be the action at particular spots, which will increase the pitting and quickly produce holes in one piece of metal, while another piece, of the same size and thickness, long remains serviceable, even if yielding the same amount of rust in a given time, because the action is uniformly distributed. This action of iron is similar to that of zinc. The latter, when pure, dissolves very slowly in acid, but when impure it dissolves readily, because of the electrolysis between the spots of pure zinc and the spots of impurities.

The fuller details of this explanation accord with the present-day theory of physical chemistry. Cushman's results confirm earlier work by Whitney, and are independently verified by Walker.

¹ Farmers' Bulletin No. 239, U. S. Department of Agriculture, p. 20.

² Applied Science, Proceedings of the Toronto Engineering Society, January, 1908, p. 125.

There may be many hundred independent local circuits on a few square feet of surface. Cushman¹ says that, in almost all modern steel woven-wire fences some wires will be found to far outlast others. It is just this point of unevenness of lasting quality in wires from successive heats in the same mill, which have practically the same chemical composition, that is hard to explain by any theory but that of galvanic or electrolytic action.

These ideas suggest the use of better steel for furnace jackets, though the fact that the rapid corrosion has occurred with jackets purchased from at least ten different manufacturers² makes it appear that better metal is hard to obtain. Moreover, in view of the satisfactory service of the outer plates, it may seem, at first thought, that the contention for better steel is not well made. But the key to this difficulty probably lies in the different histories of the inner and outer plates in the steel mill.

For years the manufacturers have fully appreciated the practical benefit of an increased amount of work put upon steel, at the proper temperature, in improving the physical properties. The National Tube Company has found that the resistance to rusting is greatly increased by similar treatment, and this company has developed a special method of applying it.³ Now the rolling of the outer plates of the water jackets to a thickness of $\frac{3}{8}$ in. necessarily requires more work than rolling the inner plates to 0.5 in. and we may therefore expect the former to be more resistant to rusting. The angle-iron stiffeners, which Mr. Lee says do not rust seriously, probably received a good deal of work. The fact that stay-bolts rusted badly at the ends next to the inner plates, while being little affected at the other ends, is explained by the electrolytic theory as follows: It is well known that rust, once formed, increases the rate of corrosion. Mr. Speller⁴ reports finding a potential as great as 50 millivolts between one clean iron and another rod exactly similar which had a very slight coat of rust, both being immersed in water. When both rods were clean, the potential was much less. The rust on the inner plates of the water jackets will set up a current between

¹ Farmers' Bulletin No. 239, U. S. Department of Agriculture, p. 21.

² Private letter from Mr. Lee.

³ Private letter from Frank N. Speller of the National Tube Co.

⁴ Applied Science, Proceedings of the Toronto Engineering Society, January, 1908, p. 125.

itself and a stay-bolt, which will corrode the latter. This current, in seeking the path of least resistance, will pass from the stay-bolt through the water and back to the rust of the inner plate without going as far as the outer plate. This effect will be decidedly less in the case of angle-iron stiffeners, because the latter do not have the intimate contact with the inner plate that the stay-bolts have, and therefore the electric current meets more resistance.

Speller found the voltage between steel and mill-scale to be greater than between the metal and ordinary rust. It may be that, for some peculiar reason, this scale is always worse on the 0.5-in. than on the $\frac{3}{8}$ -in. plate, though this is hardly probable. However, it is advisable to see that all scale and rust are thoroughly removed before the jackets are put together. I believe that the main point is the working of the metal in the mill. The steel manufacturers are making important investigations with valuable practical results, but if they do not yet supply 0.5-in. steel of suitable quality, it may be well to try jackets made wholly of $\frac{3}{8}$ -in. stock.

Arthur S. Dwight, New York, N. Y. (communication to the Secretary¹): Several times in the course of my smelter work have I experienced trouble from corrosion of blast-furnace water jackets, particularly of the wrought-iron or steel jackets commonly used in copper smelting, and in a manner very similar to that described by Mr. Lee, but, in my case, always traceable in the end to acid water.

The troubles at Douglas seem to be somewhat more aggravated than one usually encounters, and the causes more obscure. I understand that, like most of the smelters in the Southwest, the Copper Queen works has two distinct systems of water pipes, one for the regular high-pressure service, distributing fresh water to all parts of the plant, and for fire protection; while the other, at low pressure, circulates the jacket water between the blast-furnaces and a system of cooling towers. The water in the jacket circulatory system has numerous opportunities to pick up soluble sulphates, principally in the vicinity of the blast furnaces (where it is almost impossible to prevent copper flue-dust from sifting into the launders and open places in the circuit), or by flue-dust being blown into the waters of the ponds and cooling tower.

¹ Received September 7, 1908.

Although the tests for acidity in the jacket water which Mr. Lee has made from time to time have failed to show the presence of acid, and although we may perhaps properly suspect some other cause to be the principal one, I am strongly inclined to think, nevertheless, that the troubles are aggravated by the presence of acid in the water, particularly as it seems to be admitted that the corrosion is somewhat more evident in the circulatory system than it is in the service system.

The fact, however, that some pitting and corrosion also occur in the fresh-water line points to the presence of some peculiar property in the water itself. The irregularity with which some sections of pipe and some jacket sheets are corroded, while others in the vicinity, or even adjacent parts of the same piece of metal, are entirely free from attack, would point to faulty material, or perhaps careless heat treatment in the manufacture of the steel. But, granting all this, we are still far from a satisfactory answer to the riddle. The Copper Queen smelter is built of the best materials currently obtainable, purchased from various makers, and, as it stands, represents better than average modern smelter construction. The analysis of the water gives no clue; in fact, it must be said to be unusually harmless looking. The theory of electrolysis does not seem to meet the conditions. By the process of eliminating those theories which fail to satisfy, we are finally confronted with the question: can the fact that this water is raised from the deep wells by compressed air have any bearing on the problem? Is it not possible, that, by the intimate commingling of the water and air at high pressure, such thorough aeration might occur as would make the water an extraordinarily active oxidizing agent? This could easily be determined by experiment. Personally, I should consider this a surprising fact if it proved to be the correct explanation, but the logic of the situation seems to point to some such cause out of the ordinary.

In this connection, it may be pertinent to give some of my own experiences with troubles of this kind, and the remedy that was developed.

The most serious case of corrosion of pipes and water jackets I have ever had occurred while I was in charge of the operations of the Greene Consolidated Copper Company, at Cananea, Sonora, Mexico, especially during the latter part of 1905. Cananea is not more than sixty miles distant from Douglas, and there is

some similarity in the conditions of water supply to the furnaces and in the character of the ground-water, etc.

Our troubles were made the subject of a long series of studies by R. L. Lloyd, who was then superintendent of the smelting department, and to him is due the credit for finding a practical and satisfactory remedy. It seems to me proper, therefore, that he should be allowed to tell it in his own way, and I insert the following extract describing the episode in detail from a letter written by him at my request, and which I have his permission to include in this discussion: Complying with your request to give you the details of the manner in which we worked out the troubles at Cananea in connection with the serious corrosion of the water jackets and pipes in the circulatory system of the blast furnaces, I take pleasure in giving you the facts as I can recall them, though I am at a disadvantage in not having my notes on the subject accessible. I agree with you in thinking that the troubles which Mr. Lee describes as being so serious at the Douglas plant are almost identical with those which we experienced, and I think it very probable that the same remedy may correct his difficulties also.

At Cananea, the main part of the trouble occurred in the long pipe-lines which extended from the water-cooling tower to the jackets. There was also trouble in the jackets, particularly at the joints around the tuyeres. It was noticed that wherever iron and brass were in contact, as, for instance, at the brass valves, the corrosive action was greatly intensified, presumably on account of local electrolysis. The trouble at one time assumed such proportions that it became very difficult indeed to keep the pipe-lines and jackets in sufficiently good repair for steady operation, and many expedients were tried in the attempts to discover a remedy. Slaked lime was used to neutralize the acid in the water, but the results were only partly successful, and were attended with the serious disadvantages arising from the accumulation of the lime in the tanks, and the formation of lime scales on the smaller pipe-lines. We then tried crude sodium carbonate, such as we had been using to prevent scale in the boilers, which gave better results than the lime, but was still far from satisfactory. Large slabs of zinc were also connected up in various places, especially in the steel overflow-tank, in the attempt to counteract electrolysis.

After much study and experiment we finally determined the primary cause of the acid in the water to be the absorption of fumes of SO_2 by the sprayed water in the cooling tower, which was situated on the leeward side of the smelter with respect to the prevailing winds, and on top of a hill, nearly on a level with the top of the furnace building. The SO_2 gas in the smelter fumes blowing through the cooling-tower was dissolved by the falling water and slowly became oxidized, and eventually formed a dilute solution of sulphuric acid. The amount of corrosive sulphates was further augmented by the fact that more or less flue-dust got into the water system by sifting into the launders around the furnaces and under the feed floor, as is likely to happen at any smelter plant, as usually constructed. The position of the cooling tower was unfortunate, but on account of limitations of space it could not have been avoided, even if the trouble due to the smelter fumes had been anticipated.

While working hardest to correct the difficulty, which threatened to be most serious, I read an article published in pamphlet form by an author whose name I have among my notes, but unfortunately not now accessible, which mentioned the effect of arsenic salts in deterring the solubility of iron and steel in acid solutions. I was at once very much interested to know if this could possibly have any bearing on this problem, and I proceeded to "doctor" the water system with commercial arsenic oxide. The good effect of this addition was felt very quickly, and the corrosion was practically ended. From that time on, 1 kg. of arsenic oxide was added to the water system each week, and a portion of the water in the circulatory system was allowed to run to waste, being replaced by fresh water, when analyses showed that the amount of sulphates was getting high.

In this manner we were able to avoid the corrosion of the jackets. It was noticed that even when the water became appreciably acid there was little or no trouble from corrosion of the pipe system and jackets, though we always endeavored to keep the acid neutralized with commercial sodium carbonate.

It is to be regretted that Mr. Lloyd's citation of the article from which he obtained the suggestion for trying arsenic oxide cannot be made more concise at this time, but if it proves to be a matter of special interest it can doubtless be supplied later;

meantime, perhaps the paper may be known to some members of the Institute, who can complete the facts.

In this connection, it would be interesting to ascertain whether there is as much trouble experienced from corrosion of pipes and water jackets in smelting works treating large quantities of arsenical copper ores, as there is in plants like Douglas and Cananea, which treat ores exceptionally free from arsenic. It is not impossible that the arsenic fumes might automatically furnish the needed antidote for the acid in the water. Personally, I have no comparison which I can present from my own experience.

The following incident, which recently came to my attention, presents what seems to be an interesting confirmation of the deterrent action of arsenic in the corrosion of iron. A car-load of commercial sulphuric acid was purchased by a western steel works for pickling wire. The acid refused to work properly, though chemical tests showed it to be of proper strength. The steel company complained to the acid-makers, who sent an expert to investigate. He looked over the situation, promptly sent the lot back to the factory, and substituted a new lot of acid for it. Though inclined to be reticent about the cause of the trouble, the expert finally admitted to the chemist of the steel works that this particular car-load of acid had been made from pyrites containing considerable arsenic, and that there was an appreciable amount of arsenic in the acid, stating, furthermore, that had his company known the purpose for which the acid was to be used, they never would have sent the kind they did.

Corrosion of jig screens and other iron work in wet-concentration mills might also be averted by applying the arsenic remedy, though I have never heard of its being tried.

J. A. Thomson, Pullman, Wash. (communication to the Secretary¹): In reference to this pitting and corrosion in the water jackets of blast furnaces, to my mind there is no mystery or fancied "electrolytic" action in the question. It is simply an effect of the air carried by water, fed to the jackets to keep them cool and the action is as follows: As soon as the cold water comes in contact with the warm part of the jacket, it is heated and compelled to give up its air, which, being in contact with the plate, settles thereon. The circulation being sluggish, it is only

¹ Received April 27, 1908.

when the bubbles have grown sufficiently large that they rise, and this rise is hindered to some extent by the bosh. During the period of rest, the air, containing both oxygen and carbonic acid, will attack the iron, and when small irregularities have been thus formed, subsequent bubbles find still better lodgment and speedily effect the formation of pit-holes.

If the water is fed to the jacket near the bottom, and if it is saturated with air, it can be shown that every square inch of heated surface of the jacket generates about 4.5 cu. in. of air per hour, equal to about one bubble $\frac{1}{8}$ in. in diameter per-second.

The great difference of temperature between the water and the fire side of the jacket plate, with the consequent straining of the grain of the plate, quickly loosens all rust as it is formed, so that metallic iron is always exposed to the air given up by the water.

The smooth parts mentioned as having escaped this pitting may be accounted for in a number of ways. At the start, such a spot may have had some adhering slag or other substance which reduced the heat at that point, so that the first irregularities produced would be formed away from that spot, and the bubbles would be more continuously produced where they found good lodgment. Or, again, the spot may be a patch (of the kind found in all plates) which has been clean-rolled in the making. There are also various other causes. This sort of thing is a frequent occurrence in the pitting by similar causes on the furnaces of marine boilers.

The same reasoning, but reversed, will apply to the outside sheets. There is no extra heat on the outer side of the sheet, hence bubbles do not form there, but only on the hot sheet next the furnace.

As to the impellers of the rotary pumps, this case is similar to the action on a ship's propeller, in which the air is not driven out by the heat, but is abstracted by the partial vacuum formed, and in which, in spite of the high velocity of the water, there seems to be sufficient time for the mischief to be done. Even bronze blades are sometimes pitted in the same way.

My recommendation would be in the line of putting the water under pressure before admitting it to the jackets; that is, let the inlet to the jacket have a non-return valve like a large feed-check, with a stem carrying a weight, so that the pump feeding

the jacket would have to force the water against, say, 20 or 30 pounds per square inch. From under this check a small (say, $\frac{3}{8}$ in.) pipe should lead back to the well. The water being under pressure before entering the jacket, a large part of the entrained air will escape through this pipe. I do not mean the jacket to be under pressure, but only the pipe to the inlet. I have no doubt this arrangement would give much relief. I have used it many times as a remedy for pitting in marine boilers.

Of course, I presume there are no unknown acids in the water, and that is just ordinary potable water, as seems to be proved by the fact that the boilers are said not to have been attacked in any way.

With regard to the statement of George M. Douglas, his experience in the White Star boats must have been decidedly limited, or he would not talk of a little salt water causing corrosion. It is a common practice to fill new boilers with sea-water at first, for the purpose of preserving them; and when I went to sea we had no evaporation to make fresh water, and if we ran short, we made up with sea-water. I have run a ship from Hankow, China, to London, forty-three days' hard driving, without opening a cock that was not open at the start, and not a pint of fresh water to make up waste, only the sea to draw from, and at the end of the voyage the boilers were in excellent condition.

If a satisfactory way cannot be devised to introduce the water under pressure, I think that the use of nickel steel would solve the whole problem.

METAL CORROSION AND PROTECTION¹

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The following abbreviations have been used: Diag., diagrams; Dr., drawings; ed., edition; Ill., illustrations; n. d., no date; n. s., new series; no., number; p., page; pl., plate; pt., part; v., volume; w., words.

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¹ Reprinted by permission from The Monthly Bulletin for July, 1909, issued by the Carnegie Library, Pittsburgh, Pa; with additions and corrections to February, 1910.

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See also editorial, p. 343.

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Cushman, Allerton S.

Preservation of iron and steel. 32 p. 6 ill. 1909. (In Journal of the Iron and Steel Institute, v. 79, p. 33.)

Cushman, Allerton S. — *continued.*

The same. 11,000 w. Ill. 1909. (In Iron and coal trades review, v. 78, p. 735.)

The same. (In Engineering, v. 87, p. 710, 742.)

The same, slightly condensed. (In Engineer, London, v. 107, p. 537, 565.)

The same, slightly condensed. (In Ironmonger, v. 127, p. 14.)

Discussion and correspondence 4,500 w, p. 93.

Consideration of the nature and degree of protection to metals by metallic coatings, paints and cement, with applications of the electrochemical theory.

Cushman, Allerton S.

Preservation of iron and steel. 40 p. Dr. Ill. 1909. (In United States — Office of public roads. Bulletin no. 35.)

Reviews theories of corrosion and methods of protection commonly in use; and shows principles that should guide in the selection of the paint pigment to be used as coating.

Davis, R. O. E.

Corrosion of iron. 900 w. 1907. (In Chemical engineer, v. 5, p. 174.)

Experiments indicate that water and oxygen are the only essentials for corrosion.

Davis, W. A.

Rusting of iron. 4,400 w. Dr. 1907. (In Science progress in the twentieth century, v. 1, p. 408.)

Traces development of theories, concluding that rusting is caused by the action of water containing traces of acid on iron in the presence of oxygen.

Dunstan, Wyndham Rowland, and others.

Rusting of iron. 26 p. Dr. 1905. (In Journal of the Chemical Society, v. 87, pt. 2, p. 1548.)

Claims proof that for the rusting of iron the presence of oxygen and water only is necessary, and that "in the ordinary atmospheric rusting of pure iron electrolytic action does not occur."

English, F. M.

Lecture on toncan metal. 2,500 w. 1909. (In Metal worker, v. 71, June 12, p. 67.)

The same. (In Industrial world, v. 43, p. 730.)

Description of a metal with the working properties of soft steel which offers unusual resistance to corrosion. Theory of corrosion is taken up.

Fraser, Alexander G.

Relative rates of corrosion of acid and basic steel. 16 p. Folding pl. 1907. (In Journal of the West of Scotland Iron and Steel Institute, v. 14, p. 82.)

Discussion, p. 112. 20 p.

The same, condensed. 1,600 w. (In Iron age, v. 79, p. 1196.)

Tests in air, river water, salt water and sulphuric acid.

Friend, J. Newton.

Corrosion of iron. 1,500 w. 1909. (In Engineering, v. 88, p. 531.)

Paper before Iron and Steel Institute.

Claims that pure water is not sufficiently active to cause the corrosion of pure iron in the presence of oxygen alone.

Friend, J. Newton.

Rusting of iron. 28 p. Dr. 1908. (In *Journal of the Iron and Steel Institute*, v. 77, p. 5.)

Experimental results indicate that "the rusting of iron is primarily the result of acid attack" rather than of electrochemical nature, and that the hygroscopic nature of rust underlies its corrosive action.

Garrett, John Henry.

Action of water on lead; being an inquiry into the cause and mode of the action and its prevention. 116 p. 1891.

Gee, W. W. Haldane.

Electrolytic corrosion. 6,500 w. Diag. dr. 1908. (In *Electrician*, London, v. 61, p. 66, 98.)

The same, condensed. 4,500 w. (In *Electrical engineering*, London, v. 3, p. 559.)

The same, condensed. 1,300 w. (In *Electrical review*, London, v. 62, p. 692.)

Paper before the Manchester local section of the Institute of Electrical Engineers. Notes on conditions under which corrosion takes place.

Gesellschaft für Hochdruck-Rohrleitungen.

Wasserbeschaffenheit und korrosionen. 4,000 w. Ill. 1909. (In *its Rohrleitungen*, p. 127.)

Considers action of water on iron, especially of boiler-waters, and methods of protection.

Gore, G.

Influence of ordinary chemical corrosion [on voltaic action]. 5 p., n. d. (In his *Art of electrolytic separation of metals*, p. 65.)

Considers influence of kind of substance on chemical corrosion, influence of temperature on corrosion and includes table showing corrosion series of the metals at 60° F. and 160° F.

Gore, G.

On some relations of chemical corrosion to voltaic current. 10 p. 1884. (In *Proceedings of the Royal Society of London*, v. 36, p. 331.)

"Chief object of this research was to ascertain the amounts of voltaic current produced by the chemical corrosion of known weights of various metals in different liquids."

Gore, G.

Some relations of heat to voltaic and thermo-electric action of metals in electrolytes. 2,800 w. 1883. (In *Proceedings of the Royal Society of London*, v. 36, p. 50.)

Abstract. Many experiments tended to show that "the most chemically-positive metals were usually the most quickly corroded, and the corrosion . . . was usually the fastest with the most acid solutions . . . Corrosion was not the cause of pure thermo-electric action of metals in liquids."

Gore, G.

Some relations of heat to voltaic and thermo-electric action of metals in electrolytes. 40 p. Ill. 1883. (In *Proceedings of the Royal Society of London*, v. 37, p. 251.)

Examines "the relations of the thermo-electric to the chemico-electric behaviour of metals in electrolytes, and to ordinary chemical corrosion, and the source of voltaic currents."

Gruner.

Recherches sur l'oxydabilité relative des fontes, des aciers et des fers

Gruner — *continued*.

doux. 1,000 w. 1883. (In *Comptes rendus des séances de l'Académie des sciences*, v. 96, p. 195.)

Hambuechen, Carl.

Experimental study of the corrosion of iron under different conditions. 40 p. Diag. ill. 1900. (In *Bulletin of the University of Wisconsin; engineering series*, v. 2, no. 8.)

"Bibliography," p. 274.

Concludes that character and rapidity of corrosion upon physical and chemical properties of the object and that "the application of stress to metals causes an increase in chemical activity."

Hamlet, William M.

On the protection of iron and other metal work. 750 w. 1903. (In *Chemical news*, v. 88, p. 219.)

Paper before the Royal Society of New South Wales.

Brief review of theories and recent work.

Heyn, E. & Bauer, O.

Über den angriff des eisens durch wasser und wässerige lösungen. 104 p. Folding pl. 1903. (In *Mitteilungen aus dem Königlichen Material prüfungsamt*, v. 26, p. 1.)

The same, condensed. 4,800 w. (In *Stahl und eisen*, v. 28, p. 1564.)

The same, abstract translation. 400 w. (In *Journal of the Iron and Steel Institute*, v. 78, p. 663.)

Experiments to determine the cause of corrosion, the necessary active agents, the influence of contact of iron with other metals, comparative corrosion of irons of different compositions and the comparative attack of various liquids on iron.

Howe, Henry M.

Corrosion of iron. 11 p. 1895. (In his *Metallurgy of steel*, ed. 4, v. 1, p. 94.)

Considers influence of surrounding conditions and of chemical composition, and the relative values of protective coatings.

Howe, Henry M.

Relative corrosion of wrought iron and steel. 5,600 w. 1895. (In *Mineral industry*, v. 4, p. 429.)

The same, condensed. 1,600 w. (In *Journal of the Iron and Steel Institute*, v. 50, p. 427.)

Gives results both from laboratory experiments and from actual industrial use.

Howe, Henry M.

Relative corrosion of wrought iron and steel. 1,800 w. Dr. 1906. (In *Proceedings of the American Society for Testing Materials*, v. 6, p. 155.)

Discussion, 7,000 w.

The same, condensed. 1,300 w. (In *American machinist*, v. 29, p. 49.)

The same, condensed. (In *Engineering magazine*, v. 31, p. 750.)

The same, condensed. (In *Industrial world*, v. 40, p. 228.)

The same, condensed. (In *Iron age*, v. 77, 2047.)

Rapid corrosion of steel in many instances may be due to the inferior quality of the steel.

Howe, Henry M.

Relative corrosion of wrought iron, soft steel, and nickel steel. 1,500 w. Dr. 1900. (In *Engineering and mining journal*, v. 70, p. 188.)

Irvine, Robert.

On the corrosion of iron. 500 w. Dr. 1891. (In *Journal of the Society of Chemical Industry*, v. 10, p. 237.)

Attributes corrosion largely to galvanic action between dissimilar varieties of iron.

Knudson, Adolphus A.

Electrolytic corrosion of the bottom of oil tanks and of other structures. 4,300 w. Dr. Ill. 1908. (In *Transactions of the American Electrochemical Society*, v. 14, p. 189.)

Discussion, 900 w.

The same. (In *Canadian engineer*, v. 19, p. 154.)

Corrosion of oil-tanks thought to be caused by galvanic action set up by the distribution of acid or alkaline electrolytes over the iron surface.

Koller, Theodore.

Praktische erfahrungen über rostschutzmittel und deren bedeutung für die technik. 4,500 w. 1901. (In *Glaser's annalen für gewerbe und bauwesen*, v. 48, p. 161.)

Considers atmospheric action on metals and composition of many protective coverings.

Kosmann, B.

Ueber die corrosion von fluss- und schweisseisen und über den zerfall von legirungen. 2,100 w. 1893. (In *Stahl und eisen*, v. 13, pt. 1, p. 149.)

The same, condensed. (In *Journal of the Iron and Steel Institute*, v. 43, p. 399.)

Difference in resistance to corrosion of ingot and weld iron is held to be due entirely to difference in their chemical composition.

Lee, George B.

Corrosion of water-jackets of copper blast-furnaces. 500 w. 1907. (In *Transactions of the American Institute of Mining Engineers*, v. 38, p. 877.)

Brief discussion. Complete discussion will appear in succeeding volume.

Lincoln, Azariah Thomas.

Electrolytic corrosion of brasses. 38 p. Diag. ill. 1907. (In *Transactions of the American Electrochemical Society*, v. 11, p. 43.)

Experimental data and conclusions from corrosion products of brasses exposed to solutions of the more common sodium and ammonium salts.

Lincoln, Azariah Thomas, & Bartells, G. C. jr.

Additional experiments on the electrolytic corrosion of brasses. 7 p. Diag. 1908. (In *Transactions of the American Electrochemical Society*, v. 13, p. 331.)

Tests of corrosion in "synthetic sea water."

Lincoln, Azariah Thomas, and others.

Electrolytic corrosion of brasses. 36 p. Diag. 1907. (In *Journal of physical chemistry*, v. 11, p. 501.)

Experiments on the corrosion of copper-zinc brasses in normal solutions of sodium and ammonium salts.

Lindsay, Charles C.

On the corrosion and preservation of iron and steel. 32 p. Dr. 1881. (In Transactions of the Institution of Engineers and Shipbuilders in Scotland, v. 24, p. 77.)

The same, condensed. 2,000 w. (In Scientific American supplement, v. 12, p. 4570.)

Consideration of the cause and action of corrosion and methods for its prevention by coatings of paint, metal or magnetic oxid.

McAlpine, William J.

Corrosion of iron. 1,200 w. 1868. (In Transactions of the American Society of Civil Engineers, v. 1, p. 23.)

Cites instances of preservation of water-pipes, iron submerged in salt water, etc.

McBride, James.

Corrosion of steam drums. 8,000 w. Ill. 1891, 1894. (In Transactions of the American Society of Mechanical Engineers, v. 12, p. 518; v. 15, p. 1087.)

Includes lengthy discussion.

Mallet, Robert.

First report upon experiments, instituted at the request of the British Association, upon the action of sea and river water, whether clear or foul, and at various temperatures, upon cast and wrought iron. 59 p. 1839. (In Report of the eighth meeting of the British Association for the Advancement of Science, p. 253.)

Summary of knowledge of the subject to that time (1839), indicating directions in which further investigation was necessary.

Mallet, Robert.

Second report upon the action of air and water, whether fresh or salt, clear or foul, and at various temperatures, upon cast iron, wrought iron, and steel. 88 p. 1840. (In Report of the tenth meeting of the British Association for the Advancement of Science, p. 221.)

Experiments on the relative rates of corrosion of different irons in fresh and salt water and the protection of iron and steel by coatings of paint or metal.

Mallet, Robert.

Third report upon the action of air and water, whether fresh or salt, clear or foul, and at various temperatures, upon cast iron, wrought iron, and steel. 53 p. 1843. (In Report of the thirteenth meeting of the British Association for the Advancement of Science, p. 1.)

Mason, F. H.

Rusting of iron. 1,200 w. 1908. (In Mining and scientific press, v. 97, p. 329.)

Comments on conclusions of Tilden and describes original experiments in which potassium bichromate was found to retard corrosion.

Mason, William P.

Action of water upon metals; tanks, pipes, conduits, boilers, etc. 19 p. Dr. 1902. (In his Water supply, p. 394.)

Data compiled from various sources, giving references.

Milton, James Tayler.

Corrosion and decay of metals. 5,000 w. Dr. 1908. (In *Mechanical engineer*, v. 22, p. 530, 580.)

Lecture before the Institute of Marine Engineers.

Explanation of theory of corrosion, with examples. Considers corrosion as due to the action of a liquid or agent in such a way that the current leaves the metal to enter the corrosive agent.

Milton, James Tayler, & Larke, W. J.

The decay of metals. 20,800 w. Ill. 1903. (In *Minutes of proceedings of the Institution of Civil Engineers*, v. 154, p. 138.)

"In this paper the ordinary oxidation of iron and steel will not be dealt with; but a deterioration which sometimes occurs in cast iron and other metals, from causes which are to some extent obscure, will be considered."

Considers principally brass, bronzes, Muntz's metal, etc. Well illustrated with photomicrographs, etc.

Discussion and correspondence.

Moody, Gerald Tattersall.

Rusting of iron. 3,300 w. Dr. 1906. (In *Journal of the Chemical Society*, v. 89, pt. 1, p. 720.)

Challenges Dunstan's conclusions and asserts that carbonic acid must be present, in however minute quantity, before rusting begins.

Mugdan, M.

Über das rosten des eisens und seine passivität. 7,000 w. 1903. (In *Zeitschrift für elektrochemie*, v. 9, p. 442.)

The same, abstract. 250 w. (In *Journal of the Iron and Steel Institute*, v. 64, p. 720.)

Finds that rust forms more readily in solutions of nitrate, chlorid, sulphate, and perchlorate.

Murray, M. Thornton.

Rust. 5,000 w. 1908. (In *Iron and coal trades review*, v. 77, p. 2104.)

Paper before the Staffordshire Iron and Steel Institute.

Considers theories and recent developments.

Murray, M. Thornton.

Rust; its formation and prevention. 1,500 w. 1908. (In *Mechanical engineer*, v. 21, p. 679.)

The same, with comment. (In *Iron and coal trades review*, v. 76, p. 2087.)

Brief review of theories.

Newman, John.

Metallic structures; corrosion and fouling and their prevention; a practical aid-book to the safety of works in iron and steel, and of ships, and to the selection of paints for them. 374 p. 1896.

Record of author's experience, supplemented by information compiled from many sources. Omits electrolysis but considers nearly all other causes of corrosion.

Parker, William.

On the relative corrosion of iron and steel. 11,200 w. Dr. 1881. (In *Journal of the Iron and Steel Institute*, v. 18, p. 39.)

Effects of exposure in air, in sea-water, in marine boilers, etc.

Pennock, J. D. & Morton, D. A.

Commercial aqua ammonia; its effect upon iron, its impurities, and methods for determining them. 3,500 w. 1902. (In Journal of the American Chemical Society, v. 24, p. 377.)

Concludes that concentrated ammonia solutions not only do not rust clean iron but prevent its rusting in the presence of corrosive agents.

Report of committee U on the corrosion of iron and steel. 700 w. 1907. (In Proceedings of the American Society for Testing Materials, v. 7, p. 209.)

Offers suggestions as to the conditions for experiments on the connection between the rapidity of solution in acid and natural corrosion.

Report of committee U on the corrosion of iron and steel. 2,000 w. Diag. 1908. (In Proceedings of the American Society for Testing Materials, v. 8, p. 231.)

Contains specifications for tests of steel wire and remarks on the value of acid and immersion tests in determining resistance to corrosion.

Rhead, E. L.

Some probable causes of corrosion of copper and brass. 3,000 w. 1903. (In Mechanical engineer, v. 24, p. 525.)

Paper before the Institute of Metals.

Gives instances of actual corrosion of brass and copper in use, with only suggestions as to causes.

Rhodin, John G. A.

Corrosion of copper and copper alloys. 9,000 w. Diag. dr. 1907. (In Engineer, London, v. 104, p. 53, 75, 106.)

See also editorial, p. 63.

Considers alloys as balanced or unbalanced, of which the former have the better mechanical properties. Regards the unbalanced alloys as having a voltaic combination formed.

Rhousopoulous, O. A.

Über die reinigung und konservierung der antiquitäten. 1,900 w. 1905. (In Chemiker zeitung, v. 29, pt. 2, p. 1198.)

Discusses the corrosion and cleaning of Greek antiquities.

Richards, Theodore William, & Behr, G. E. jr.

Electromotive force of iron under varying conditions, and the effect of occluded hydrogen. 43 p. Diag. dr. 1906.

Takes issue (p. 20) with conclusion that corrosion is necessarily increased by stress.

Rudeloff, M.

Bericht über vergleichende untersuchungen von schweisseisen und flusseisen auf widerstand gegen rosten. 125 p. Ill. 1902. (In Mittheilungen aus den Königlichen Technischen Versuchsanstalten, v. 20, p. 83.)

The same, condensed. 4,000 w. (In Stahl und eisen, v. 23, p. 384.)

The same, abstract. 1,500 w. (In Journal of the Iron and Steel Institute, v. 63, p. 713.)

Extensive experiments on the relative resistance to corrosion of wrought-iron and steel, considering the effect of different conditions and coatings and giving the relative corrosive action of various agencies.

Rudeloff, M.

Untersuchungen über die widerstandsfähigkeit von seildrähten gegen

Rudeloff, M. — *continued.*

rosten. 4,000 w. Ill. 1900. (In *Mitteilungen aus den Königlichen Technischen Versuchsanstalten*, v. 18, p. 107.)

Results of many tests on the mechanical properties of rusted wire. Numerous tables and diagrams.

Rust and paint researches. 1,200 w. 1909. (In *Engineering record*, v. 59, p. 674.)

Editorial outline of value of experiments and theories of Cushman and Walker.

Rusting of iron. 3,500 w. 1908. (In *Engineering*, v. 85, p. 329.)

Editorial review of theoretical and experimental work.

Rusting of iron. 1906-07. (In *Nature*, v. 74, p. 540, 564, 586, 610; v. 75, p. 31, 390, 438, 461.)

Letters by Friend, Moody, Richardson, Meehan, Dunstan, and Stromeyer concerning the theory of rusting and the action of carbon dioxide.

Rusting of iron and the Rochester, N. Y., steel conduit. 3,500 w. 1909. (In *Engineering*, v. 88, p. 272, 304.)

Review of work and conclusions of many recent investigators of the cause of corrosion.

Sang, Alfred.

Corrosion of iron and steel. 49 p. 1909. (In *Proceedings of the Engineers' Society of Western Pennsylvania*, v. 24, p. 493.)

Discussion, 21 p.

Comprehensive treatment of the subject, tracing the development of the theory of corrosion and methods for its prevention. References given in full.

Schleicher, A. & Schultz, G.

Untersuchungen über das rosten von eisen. 2,400 w. Diag. 1908. (In *Stahl und eisen*, v. 28, p. 50.)

Experiments on the differences of potential of metal plates separated from one another in water.

Sebelien, John.

Über die korrosion und die reinigung metallischer antiquitäten. 1,200 w. 1906. (In *Chemiker zeitung*, v. 30, pt. 1, p. 56.)

Refers to work of Axel Krefling in cleaning rusted antiquities by the reducing action of nascent hydrogen.

Sexton, A. Humboldt.

Corrosion and protection of iron and steel. 11 p. 1900. (In his *Chemistry of the materials of engineering*, p. 132.)

Sexton, A. Humboldt.

Corrosion and protection of metals. 147 p. 1906?

Treats of corrosion of iron, steel, lead, zinc, copper, etc., and protection both by paints and metallic coatings.

"Useful and generally accurate summary of present knowledge."

Review. 1,000 w. (In *Engineering news*, v. 56, p. 184.)

Speller, Frank N.

Corrosion of iron and steel. 900 w. 1907. (In *Proceedings of the Engineers' Society of Western Pennsylvania*, v. 22, p. 472.)

The same. (In *Iron age*, v. 79, p. 478.)

Discussion, 1,800 w.

Gives results of tests showing steel to be superior to wrought-iron.

Speller, Frank N.

Puddled iron versus soft steel. 2,200 w. Ill. 1905. (In *Iron age*, v. 75, p. 1666, 1881.)

Claims equal resistance of iron and steel to corrosion, in reply to statements of Roe.

Spencer, Thomas G.

Deterioration of lead sheaths of aerial and underground telephone cables, 4,000 w. Ill. 1909. (In *Telephony*, v. 17, p. 216.)

Abstract. Considers causes of deterioration under six heads: (1) Mechanical injury; (2) Chemical decomposition; (3) Electrolysis; (4) Vibration; (5) Lightning; (6) Impurities in the lead. Author is chemist to Stromberg Carlson Telephone Mfg. Co., which has printed this paper for free distribution to its customers.

Spurrier, Harry.

Oil corrosion in cylinders. 1,200 w. 1906. (In *Power*, v. 26, p. 403.)

Effect on cast-iron, brass and bronze, of butyric acid, etc.

Stoughton, Bradley.

Corrosion of iron and steel. 15 p. Ill. 1908. (In his *Metallurgy of iron and steel*, p. 422.)

"References on corrosion," p. 436.

Thurston, Robert H.

Properties of iron and steel. 2,500 w. 1901. (In his *Materials of engineering*, ed. 8, revised, pt. 2, p. 328.)

The same. 1,200 w. 1885. (In his *Text-book of the materials of construction*, p. 210.)

Discusses corrosion, durability and preservation of iron and steel.

Thwaite, Benjamin Howard.

Coefficients of corrosion of iron and steel. 400 w. 1880. (In *Journal of the Iron and Steel Institute*, v. 17, p. 667.)

Abstract of paper showing effects of corrosion under various conditions. Shows danger of contact of different metals.

Tilden, William Augustus.

Rusting of iron. 3,500 w. Dr. 1908. (In *Journal of the Chemical Society*, v. 93, p. 1356.)

Shows that carbonic acid is not necessary to corrosion, but that it hastens the action and that rusting is due initially to electrolytic action, resulting in the production of ferrous hydroxide or carbonate.

Traube, Moritz.

Ueber die langsame verbrennung des kupfers bei gegenwart verdünnter schwefelsäure oder einer lösung von kohlen säurem ammon. 800 w. 1885. (In *Berichte der Deutschen Chemischen Gesellschaft*, v. 18, pt. 2, p. 1887.)

Hydrogen peroxide is formed in the slow oxidation of copper in presence of dilute sulphuric acid or ammonium carbonate.

Traube, Moritz.

Ueber die mitwirkung des wassers bei der langsamen verbrennung des zinks, bleis, eisens und palladiumwasserstoffs. 3,400 w. 1885. (In *Berichte der Deutschen Chemischen Gesellschaft*, v. 18, pt. 2, p. 1877.)

Author's theory is that in slow oxidation of metals water is decomposed with formation of hydrogen peroxide and that nascent oxygen cannot be formed simultaneously.

Turner, Thomas.

Corrosion of iron and steel. 20 p. 1908. (In his *Metallurgy of iron*, ed. 3, p. 413.)

Review of old and new theories and methods of prevention, with abundant references to other works.

Walker, William H.

Corrosion of iron and steel, and modern methods of preventing it. 3,000 w. 1909. (In *Engineering record*, v. 59, p. 222.)

Abstract of paper before Boston Society of Arts.

Considers theory of prevention, and satisfactory conditions attainable.

Walker, William H.

Detection of pin-holes in tin plate. 1,200 w. Ill. 1909. (In *Journal of industrial and engineering chemistry*, v. 1, p. 295.)

Plate is covered with a gelatine coating containing potassium ferricyanide. Where pin-holes exist, the iron is attacked and blue spots appear in the gelatine coating.

Walker, William H.

Electrolytic theory of the corrosion of iron and its applications. 12 p. 4 Ill. 1909. (In *Journal of the Iron and Steel Institute*, v. 79, p. 69.)

The same. 4,000 w. Ill. 1909. (In *Iron and coal trades review*, v. 78, p. 749.)

The same. (In *Engineering*, v. 87, p. 708.)

The same. (In *Mechanical engineer*, v. 23, p. 677.)

The same, condensed. 1,100 w. (In *Ironmonger*, v. 127, p. 13.)

Discussion and correspondence, 4,500 w., p. 93.

Walker, William H.

Functions of oxygen in the corrosion of metals. 5,000 w. 1908. (In *Transactions of the American Electrochemical Society*, v. 14, p. 175.)

The same, condensed. 1,700 w. (In *Electrochemical and metallurgical industry*, v. 7, p. 150.)

Considers the corrosion of zinc-plated iron wire and of tubes and shells of steam-boilers.

Walker, William H.

Protection of iron and steel from corrosion. 6,000 w. Ill. 1909. (In *Engineering magazine*, v. 37, p. 198.)

Treats of the ionic nature of corrosion and the method of observing its progress and location by means of indicators.

Walker, William H. & Dill, Colby.

Effect of stress upon the electromotive force of soft iron. 4,600 w. Diag. dr. 1907. (In *Transactions of the American Electrochemical Society*, v. 11, p. 153.)

The same condensed. 1,800 w. (In *Electrochemical and metallurgical industry*, v. 5, p. 270.)

See also editorial, p. 254.

Experimental results tend to show that differences of potential are not necessarily the result of stress.

Walker, William H. & Dill, Colby.

Influence of stress upon the corrosion of iron. 3,100 w. Diag. 1907. (In *Proceedings of the American Society for Testing Materials*, v. 7, p. 229.)

Discussion, 500 w.

Walker, William H. and others.

Corrosion of iron and steel. 5,600 w. 1907. (In Journal of the American Chemical Society, v. 29, p. 1251; v. 30, p. 473.)

The same. (In Chemical news, v. 97, p. 31, 40.)

Indicates that iron dissolves in water in the absence of both carbon dioxide and oxygen, and that on the surface of iron exposed to corrosion there is a marked difference in potential on different areas.

Wemlinger, J. R.

Development and use of steel sheet piling, with some data on the preservation of steel buried in the ground. 3,300 w. 1909. (In Engineering-contracting, v. 31, p. 406.)

Whitney, W. R.

Corrosion of iron. 5,000 w. Dr. 1903. (In Journal of the American Chemical Society, v. 25, pt. 1, p. 394.)

Emphasizes fact that the effect of carbonic acid on corrosion is cyclic and that under favoring conditions "even a trace of carbonic acid may dissolve an unlimited quantity of iron."

Williams, F. H.

Influence of copper in retarding corrosion of soft steel and wrought iron. 400 w. 1900. (In Proceedings of the Engineers' Society of Western Pennsylvania, v. 16, p. 231.)

Indicates that presence of copper retards corrosion.

Zinnpest, 1,800 w. Ill. 1909. (In Dinglers polytechnisches journal, v. 324, p. 90.)

Investigations of Cohen on alteration forms of tin and corrosive effects.

CORROSION BY ELECTROLYSIS

This section includes only destructive action of stray currents from street-railways. For other articles on electrolytic corrosion see under Corrosion, General and theoretical, and Protection, Cement, and concrete.

Abbott, Arthur Vaughan.

Electrolysis from railway currents 4,200 w. Ill. 1899. (In Casier's Magazine [electric railway number], v. 16, p. 371.)

Popular, well illustrated article.

Adams, Alton D.

Prevention of electrolysis. 3,000 w. 1900. (In Municipal engineering, v. 18, p. 1.)

Cause, injurious effects, and urgent need of preventive measures.

American Gas Institute.

Committee on electrolysis; conclusions of committee and reprints of papers. 35 p. Dr. 1908.

For previous report see American Gas Light Association.

Includes conclusions from previous report and reprints of papers by Ganz.

American Gas Institute.

Report of committee on electrolysis. 165 p. 1906. (In Proceedings of the American Gas Institute, v. 1, p. 761.)

Same as report of the American Gas Light Association.

American Gas Light Association.

Report of committee on electrolysis. 173 p. Dr. 1906.

"This report is limited to the consideration of direct-current electricity, and is, therefore, contingent upon future developments in the use of alternating-current electricity for traction purposes." *Introductory note.*

"Committee advances no new theories and can suggest no new remedies. It avoids controversial treatment and deals solely with the indisputable facts that have been developed by experience. To this end the Committee's endeavor has been to establish authoritatively the universal state of the art of electric traction with reference to electrolysis."

Report consists of five sections: (1) Theory of electrolytic corrosion; (2) Electrolysis in America; (3) Electrolysis in Great Britain; (4) Electrolysis in Germany; (5) Summary and conclusions.

Barbillion, A.

Forme du potentiel dans les rails servant au retour de courant. 800 w. 1899. (In *L'Éclairage électrique*, v. 21, p. 94.)

Theoretical, using calculus.

Bates, Putnam A.

Guarding against electrolysis of underground pipes. 3,300 w. 1906. (In *Engineering record*, v. 54, p. 122.)

The same. (In *Railroad gazette*, v. 41, p. 185.)

The same, condensed. 2,400 w. (In *Electrical review*, New York, v. 47, p. 737.)

Tests by author show that wrought-iron or lead service pipes are more susceptible than cast-iron mains. Deals fully with cause and effect of stray currents and briefly with methods of protection. Considers complete metallic circuit to be only satisfactory solution, but mentions several less efficient remedies.

Beadle, Alec A.

Electrolytic corrosion in underground pipes. 1,200 w. 1905. (In *Electrical review*, New York, v. 46, p. 19.)

Effect of stray currents and methods of prevention.

Bericht des Erdstromkommission [des Deutschen Vereins von Gas-und Wasserfachmännern]. 3,600 w. 1906. (In *Journal für gasbeleuchtung und wasserversorgung*, v. 49, p. 620.)

The same, translated. 1,500 w. (In *Electrician*, v. 57, p. 533.)

Tables and data showing conditions in many German cities.

Blake, Lucien I.

Electrolysis at Kansas City, Kan. 3,600 w. Ill. 1899. (In *Engineering record*, v. 40, p. 239.)

Lengthy report.

Blake, Lucien I.

Electrolysis of cast-iron water-mains. 1,300 w. 1899. (In *Electrical world and engineer*, v. 34, p. 934.)

Bonding of city water and gas mains to prevent electrolysis. 1,200 w. 1908. (In *Industrial world*, v. 82, p. 104.)

Contains statement of chief of Electric bureau of Philadelphia, describing excellent results obtained from bonding of mains in that city.

Brigden, W. W.

Electrolysis of water and gas pipes. 4,200 w. 1901. (In *Municipal engineering*, v. 20, p. 287.)

Plea for double trolley as the only reliable remedy.

British view of electrolysis. 1,600 w. 1900. (In *Engineering record*, v. 42, p. 41.)

Gives protective regulations passed by Parliament and by Board of Trade.

Brophy, William.

Electrolysis. 3,500 w. 1896. (In *Electrical review*, New York, v. 28, p. 276.)

Causes of metal corrosion and methods of prevention.

Brophy, William, & Gray, A. R.

Insulating couplings for protecting pipe systems from electrolysis. 1,600 w. 1904. (In *American gas light journal*, v. 80, p. 91.)

Two letters favoring their use.

Brown, Harold P.

Electrolysis of cast-iron water pipes at Dayton, Ohio. 3,400 w. 1898. (In *Municipal engineering*, v. 16, p. 84.)

The same, condensed. 2,500 w. (In *Street railway journal*, v. 14, p. 785.)

General results of more than 2,500 electrical measurements, with practical suggestions for remedy and prevention.

Brown, Harold P.

Latest method of electrolysis prevention. 2,200 w. Ill. 1897. (In *Electrical engineer*, New York, v. 24, p. 350.)

Brief comparison of European and American systems, and description of system designed by author. Insulated return conductor is used and in this case made from old rails at one-sixth the cost of copper.

Brown, Harold P.

Method of permanently protecting underground pipes from electrolytic corrosion. 2,800 w. Dr. 1895. (In *Street railway review*, v. 5, p. 157.)

Successful method of pipe protection must solve following problems: to keep pipes at least one volt negative to rails; to diminish flow of current on pipes; to secure permanent non-oxidizable contact of low resistance between pipes and necessary feeder wires.

Brownell, E. E.

Electrolysis from facts and figures. 3,500 w. Ill. 1900. (In *Journal of the New England Water Works Association*, v. 14, p. 363.)

Considers trouble entirely due to defective construction of electric railways. Suggests remedies.

Burgess, C. F.

Boiler corrosion as an electrochemical action. 23 p. Diag. Ill. 1909. (In *Journal of the Western Society of Engineers*, v. 14, p. 375.)

With discussion.

Research in the chemical engineering laboratories of the University of Wisconsin to investigate some of the peculiar conditions of corrosion encountered in operation of locomotive boilers.

Claude, M. G.

Ueber den verlauf der rückströme von strassenbahnen und über ihre

Claude, M. G. — *continued.*

elektrolytischen wirkungen. 2,000 w. Dr. 1902. (In *Elektrotechnische zeitschrift*, v. 23, p. 68.)

Abstract.

Corrosion of iron. 9,600 w. 1908. (In *Transactions of the American Electrochemical Society*, v. 14, p. 151.)

General discussion, opened by A. F. Ganz, on the corrosion of underground structure. He suggests five questions that must be solved.

Court decision as to responsibility for damage by electrolysis to gas mains. 1,300 w. 1901. (In *Engineering news*, v. 45, p. 12.)

Holds street-railways responsible for negligence.

Davis, F. A. W.

Electrical current. 3,000 w. Ill. 1901. (In *Journal of the New England Water Works Association*, v. 15, p. 225.)

Illustrated discussion of damages to underground pipe. Claims that patent pipe coatings are no protection against electrolysis.

Davis, F. A. W.

Electrolysis. 24 p. Ill. 1899.

Appendix, 15 p.

Paper before the Central States Water Works Association.

Consideration of extent of damage due to electrolysis, with data from many cities.

Davis, F. A. W.

Electrolysis in American cities. 3,400 w. Ill. 1899. (In *Municipal engineering*, v. 17, p. 349.)

Twenty illustrations showing ravages of electrolysis.

Dawson, Philip.

Return circuit; electrolytic action. 3,000 w. Ill. 1897. (In his *Electric railways and tramways*, p. 36.)

Considers damages due to and methods of checking electrolysis.

Deterioration of structural steel by corrosion and electrolysis. 2,800 w. Ill. 1906. (In *Architects' and builders' Magazine*, v. 8, p. 33.)

From a paper by James B. Cook before the Memphis Engineering Society.

Emphasizes especially the dangers of corrosion in buildings of the steel skeleton type.

Elder, J.

Untersuchungen des einflusses der vagabundirenden ströme elektrischer strassenbahnen auf erdmagnetische messungen. 5,300 w. Ill. 1900. (In *Elektrotechnische zeitschrift*, v. 21, p. 193.)

Electric traction troubles. 1,400 w. 1900. (In *Nature*, v. 63, p. 83.)

Account of stray current disturbances in England.

Electrolysis. 2,400 w. Dr. 1905. (In *International library of technology*, *Electric railways*, §39, p. 18.)

The same, condensed. 1901. (In same, *Electrical engineering*, v. 4, §23, p. 25.)

Electrolysis. 5,800 w. Dr. Ill. 1906. (In *Journal of the New England Water Works Association*, v. 20, p. 34.)

Topical discussion, in which experiences in Cambridge, New Bedford, etc., are given.

Electrolysis from electric railway return currents. 500 w. 1895. (In *Electrical world and engineer*, v. 27, p. 136.)

Refers to article in "Pittsburg leader" giving conditions in Pittsburg. Discusses methods of prevention.

Electrolysis in Providence, R. I. 3,000 w. Ill. 1900. (In *Engineering record*, v. 42, p. 106.)

Abstract and comments on report by A. A. Knudson and others.

Electrolysis of gas and water mains. 500 w. 1903. (In *New international encyclopædia*, v. 6, p. 623.)

Electrolysis of underground pipes in Brooklyn. 1,300 w. 1894. (In *Street railway journal*, v. 10, p. 169.)

Electrolysis of water mains in Dayton, Ohio. 1,000 w. 1898. (In *Engineering record*, v. 38, p. 442.)

Summary of examinations and reports by Harold P. Brown, E. E. Brownell and others.

Electrolysis of water mains in Newark, N. J. 2,200 w. 1908. (In *Engineering record*, v. 58, p. 548.)

Investigation by an expert of cause and amount of corrosion, with recommendations.

Elektrolytische zerstörungen durch vagabundierende ströme. 1,750 w. 1901. (In *Journal für gasbeleuchtung und wasserversorgung*, v. 44, p. 801, 802.)

Extracts from "Gas world," giving many methods of dealing with stray currents.

Ellicott, E. B.

Protection of water pipe from electrolysis. 7,500 w. Ill. 1901. (In *Journal of the Western Society of Engineers*, v. 6, p. 529.)

Discussion.

Farnham, Isaiah H.

Destructive effect of electrical currents on subterranean metal pipes. 9,800 w. Ill. 1894. (In *Transactions of the American Institute of Electrical Engineers*, v. 11, p. 191.)

Discussion.

Fernie, F.

Notes on the corrosion of lead-covered cables. 2,700 w. Diag. 1907. (In *Electrical engineering*, London, v. 1, p. 1037.)

Considers theory of corrosion by electrolysis, with experimental data and special cases.

Fleming, J. A.

Die elektrolytische korrosion von wasser- und gasleitungen durch die rückleitungsströme der elektrischen bahnen. 3,700 w. Dr. 1898. (In *Zeitschrift für elektrochemie*, v. 5, p. 241.)

Fleming, J. A.

On the electrolytic corrosion of water and gas pipes by the return currents of electric tramways. 6,000 w. Dr. 1898. (In *Electrician*, v. 41, p. 689.)

The same. (In *Electrical engineer*, London, v. 28, n. s. v. 22, p. 290.)

Deals with causes and conditions of injurious electrolysis but does not consider remedies.

Folwell, A. Prescott.

Pipes and conduits; prevention of deterioration. 1,000 w. 1900. (In his *Water-supply engineering*, p. 527.)

Considers briefly the injurious effects of stray currents.

French opinion of electrolysis of pipes. 1,600 w. 1901. (In *Engineering record*, v. 43, p. 515.)

Claims that no injurious effects will occur where difference of potential between pipes and rails is less than one to one and one-half volts.

Gaines, Richard H.

Corrosion of the steel water supply conduit at Rochester, N. Y. 10,000 w. Dr. Ill. 1908. (In *Engineering news*, v. 59, p. 578.)

See also editorial, p. 593, and letter by A. H. Sabin, p. 673.

Gaines, Richard H.

Electrochemical corrosion of the Rochester steel conduit. 41 p. 1908. (In *Transactions of the American Electrochemical Society*, v. 13, p. 55.)

Discussion, 6 p.

"Caused by electrolysis, the current for which resulted from chemical processes between water solutions in the soil and the metal."

Gaisberg, S. freiherr v.

Rückleitungsnetz der elektrischen strassenbahnen in Hamburg. 3,200 w. Ill. 1903. (In *Elektrotechnische zeitschrift*, v. 24, p. 492.)

Describes preventive measures.

Ganz, Albert F.

Electrolysis. 5,000 w. Dr. 1907. (In *Proceedings of the American Gas Institute*, v. 2, p. 653.)

Particular attention is paid to current measurements and to the location of the path of stray currents.

Ganz, Albert F.

Theory of electrolytic corrosion. 1,400 w. 1908. (In *Sibley journal of engineering*, v. 23, p. 10.)

From a pamphlet by the American Gas Institute, committee on electrolysis.

Simple presentation of theory of electrolysis and the part played by stray current.

Gray, John.

Electrolytic action of return currents in electrical trainways. 2,000 w. 1896. (In *Electrical review*, London, v. 38, p. 3.)

[**Haber, F.**]

Dr. Haber's report on electrolysis at Karlsruhe. 4,000 w. Dr. 1906. (In *Journal of gas lighting*, v. 95, p. 578.)

Haber, F.

Die vagabundierenden strassenbahnströme und die durch sie bedingte gefährdung des rohrnetzes in der stadt Karlsruhe i. B. 7,900 w. Ill. 1906. (In *Journal für gasbeleuchtung und wasserversorgung*, v. 49, p. 637.)

Description of electrical and electrochemical phenomena of stray currents; methods of detection and measurement; conditions existing in Karlsruhe.

Haber, F. & Goldschmidt, F.

Der anodische angriff des eisens durch vagabundierende ströme im erdreich und die passivität des eisens. 25 p. Dr. 1906. (In Zeitschrift für elektrochemie, v. 12, p. 49.)

The same, condensed. 2,100 w. (In Elektrotechnische zeitschrift, v. 28, p. 794.)

The same, condensed. 1,600 w. (In Electrician, v. 57, p. 931.)

Extensive experimental investigation of corrosion of iron electrodes by electric currents.

Haber, F. & Goldschmidt, F.

Effect of earth return current on iron pipes. 1,600 w. Dr. 1906. (In Electrical review, London, v. 59, p. 446.)

See also editorial, p. 442.

Haskell, John C.

Electrolysis. 3,000 w. 1896. (In Journal of the New England Water Works Association, v. 10, p. 278.)

Conditions in Lynn, Mass.

Discussion.

Hayden, J. L. R.

Alternating-current electrolysis. 8,000 w. 1907. (In Transactions of the American Institute of Electrical Engineers, v. 26, pt. 1, p. 231.)

Discussion, p. 264. 16,000 w. Diag. dr.

Tests "to determine . . . to what extent alternating currents passing between any metallic conductor and the ground would produce electrolytic corrosion."

Herd, Louis A.

Electrolysis of Winnipeg water mains. 3,000 w. Ill. 1909. (In Canadian engineer, v. 18, p. 197.)

Detailed report of extent of damage caused by stray currents, and recommendations for remedying the trouble.

Herrick, Albert B.

Electrolysis. 900 w. Ill. 1901. (In his Electric railway handbook, p. 310.)

Outlines briefly the theory of current distribution and electrolysis.

Herrick, Albert B.

Electrolysis. 2,000 w. 1901. (In Street railway review, v. 11, p. 37.)

History, chemistry and prevention.

Herrick, Albert B.

Electrolysis as caused by the railway return current. 7,300 w. Dr. 1904. (In Street railway journal, v. 23, p. 516.)

Presents methods of testing and most successful remedies.

Herrick, Albert B.

Electrolysis from the ground return current of street railways. 4,000 w. Ill. 1900. (In Street railway journal, v. 16, p. 472.)

Causes, detection and remedies.

Herrick, Albert B.

Ground current of electric railways, 3,000 w. Dr. 1898. (In Engineering magazine, v. 15, p. 451.)

Discussion of the causes and effects of electrolysis. Considers best preventive measures to be judicious bonding and intelligent use of feeders.

Herrick, Albert B.

Methods of determining the resistance of the railway feeder circuits and the ground return losses. 1,300 w. Dr. 1898. (In Street railway journal, v. 14, p. 186.)

Herrick, Albert B.

Some fallacies regarding electrolysis. 4,400 w. Dr. 1898. (In Street railway journal, v. 14, p. 775.)

Considers physical and electrical conditions necessary to the existence of electrolysis, tests, remedies and the attitude of electric railway companies.

See also editorial, p. 789.

Hewitt, Charles.

Return circuits of electric railways, 3,000 w. 1896. (In journal of the Franklin Institute, v. 142, p. 51.)

The same, condensed. (In Electrical world and engineer, v. 28, p. 49.)

Explains destructive electrolysis and preventive devices.

Hoopes, Maurice.

Notes on pipe electrolysis. 1,400 w. Dr. 1895. (In Electrical world and engineer, v. 25, p. 603.)

Makes use of a graphical method, which in the author's opinion presents the various phases in a clearer way than any other.

Humphreys, W. H.

Electrolysis in water-pipes. 6,500 w. 1902. (In Electrical engineer, London, v. 36, n. s. v. 30, p. 189.)

Favors double wire system, and in its absence advocates connecting negative terminal of dynamo to pipe lines.

Humphreys, W. H.

History of the electrolysis question. 7,500 w. 1902. (In Journal of gas lighting, v. 80, p. 336.)

Jackson, Dugald, C.

Corrosion caused by railway return currents. 750 w. 1896. (In Electrical world and engineer, v. 28, p. 684.)

Experiments to determine injurious effects on iron and lead. Claims that corrosion occurs wherever a current leaves a pipe or cable covering, however small the difference of potential may be.

Jackson, Dugald C.

Corrosion of iron pipes by the action of electric railway currents. 7,000 w. 1894. (In Journal of the Association of Engineering Societies, v. 13, p. 509.)

Discussion.

The same, condensed. (In Street railway journal, v. 10, p. 566.)

Jenkins, E. H.

Electrolysis. 1,000 w. 1900. (In Street railway review, v. 10, p. 260.)

Chiefly preventive measures.

Kallmann, Martin.

Administrative und sicherheitstechnische regulative für elektrische starkstromvertheilungsanlagen in den strassen des stadtgebietes Berlin. 10,800 w. Dr. 1895. (In Elektrotechnische zeitschrift, v. 16, p. 211.)

Kallmann, Martin.

Isolationskontrollsystem zur direkten anzeige von stromentweichungen. 7,200 w. Dr. 1898. (In *Elektrotechnische zeitschrift*, v. 19, p. 683.)

Kallmann, Martin.

System zur kontrolle der vagabondirenden ströme elektrischer bahnen. 10,000 w. 1899. (In *Elektrotechnische zeitschrift*, v. 20, p. 163.)

Deals largely with methods of measurement.

Kapp, Gisbert.

Verminderung der vagabundirenden erdstrome bei elektrischen bahnen. 1,800 w. 1896. (In *Elektrotechnische zeitschrift*, v. 17, p. 43.)

Plea for increased number of feeders.

Kintner, S. M.

Alternating-current electrolysis? 1,000 w. Ill. 1905. (In *Electric journal*, v. 2, p. 66S.)

Records experiments of the electrolysis of wrought-iron and lead pipe buried for one year. No appreciable action took place on the iron plates and very slight action on the lead.

Knudson, Adolphus, A.

Cause and effect of electrolytic action upon underground piping systems. 11,200 w. Ill. 1901. (In *Journal of the New England Water Works Association*, v. 15, p. 244.)

The same condensed. (In *Engineering record*, v. 43, p. 322.)

Advocates double trolley system as the only remedy.

Knudson, Adolphus A.

Corrosion of metals by electrolysis. 6,000 w. Ill. 1903. (In *Transactions of the American Electrochemical Society*, v. 3, p. 195.)

The same. 5,000 w. (In *Electricity*, v. 24, p. 217, 230.)

With reference to stray currents and injurious effects. Deals largely with testing, giving history of surveys in vicinity of New York City.

Discussion.

Knudson, Adolphus A.

Corrosion of metals underground by electrolysis. 4,000 w. Ill. 1909. (In *Journal of the Franklin Institute*, v. 168, p. 132.)

Comprehensive, general treatment of causes and effects.

Knudson, Adolphus A.

Effect of joint resistance on railway electrolysis. 1,400 w. Dr. 1900. (In *American electrician*, v. 12, p. 119.)

Shows that electrolysis is not always prevented by the independent return and advocates double overhead or underground construction as the only perfect method.

Knudson, Adolphus A.

Electrolysis in Jersey City. 1,700 w. Ill. 1899. (In *Engineering record*, v. 39, p. 233.)

Report giving many tests and recommending more frequent tap connections from return wire to rails.

Knudson, Adolphus A.

Electrolytic corrosion of water-pipes at Bayonne, N. J. 3,000 w. Ill. 1904. (In *Engineering news*, v. 52, p. 437.)

Rapid corrosion of steel and lead pipes.

Knudson, Adolphus A.

Lead-covered cables a cause of electrolysis upon gas and water pipes. 2,200 w. 9 Dr. 1 Ill. 1909. (In Journal of the New England Water-Works Association, v. 23, p. 164.)

Knudson, Adolphus A.

Remedies for electrolysis. 2,400 w. Ill. 1906. (In Cassier's magazine, v. 30, p. 337.)

Double trolley is a complete cure, but most of the attempts have been merely palliative. The following are considered: (1) More perfect bonds at the joints and improving the track return by auxiliary copper feeders; (2) making pipes part of return circuit by bonding to rails or direct to power-house negatives; (3) insulating pipes from the ground; (4) insulating joints in mains.

Krohn, Sigvald.

Ueber messungen der elektrischen ströme in den städtischen rohrlösungen. 2,000 w. Dr. 1901. (In Elektrotechnische zeitschrift, v. 22, p. 269.)

Langmuir, Irving.

Relations between polarization and the corrosion of iron pipes by stray currents. 5,200 w. Diag. dr. 1907. (In Stevens Institute indicator, v. 24, p. 348.)

Experiments with unprotected pipes and with pipes buried in lime and in cement.

Larsen, Absalon.

Ueber den elektrolytischen angriff elektrischer ströme auf eisenröhren in erde und die dabei auftretende polarisation. 1,200 w. 1902. (In Elektrotechnische zeitschrift, v. 23, p. 841.)

Larsen, Absalon.

Ueber periodische stromwendung als mittel zur verringerung elektrolytischer zerströrungen durch vagabundirende ströme. 1,900 w. Ill. 1902. (In Elektrotechnische zeitschrift, v. 23, p. 868.)

Gives illustration of gas-pipes which were subjected to tests showing that periodically reversing the current tends to diminish the destructive effects of stray currents.

Leybold, W.

Destruction of gas-pipes by means of electricity. 3,500 w. 1901. (In Electrical engineer, London, v. 24, n. s. 28, p. 372.)

Liability of reinforced concrete to electrolytic damage. 1,600 w. 1907. (In Engineering news, v. 57, p. 328.)

Editorial consideration of Knudson's experiments, indicating lines for further investigation.

Low, George P.

Rail bonding and its bearing on electrolytic corrosion. 4,500 w. Ill. 1894. (In Transactions of the American Institute of Electrical Engineers, v. 11, p. 857.)

Considers the elimination of electrolytic corrosion to be dependent on judicious bonding.

McGowan, H. E.

Electrolysis; the effect of stray trolley currents. 1,800 w. Ill. 1901. (In Stevens Institute indicator, v. 18, p. 163.)

McGowan, H. E. — *continued.*

Relief found in coating all wrought-iron pipe with a paint composed chiefly of coal-tar and rubber; also in connecting the pipes to the rails where the former are positive.

McLeary, Samuel H.

An interesting case of electrolysis. 800 w. Ill. 1906. (In *Electrical age*, v. 37, p. 273.)

Electric railway in Porto Rico on which stray currents caused very rapid corrosion, especially at point of contact between rails and spikes.

Maury, Dabney H.

Electrolysis of underground metal structures. 22 p. Ill. 1900.

Bound with Report of the special committee on electrolysis, American Water Works Association.

The same, condensed. 5,800 w. (In *Engineering news*, v. 44, p. 38.)

The same, condensed. 2,900 w. (In *Street railway review*, v. 10, p. 433.)

The same, condensed. 1,700 w. (In *Engineering record*, v. 41, p. 467.)

Maury, Dabney H.

Surveys for electrolysis and their results. 6,000 w. 1903. (In *Engineering news*, v. 50, p. 74.)

Purpose of surveys, instruments, methods and results.

Method of checking electrolysis of gas and water pipes. 700 w. Dr. 1895. (In *Street railway journal*, v. 11, p. 603.)

Method of Harold P. Brown. Pipes are connected with negative pole of dynamo, connections with pipe and rail bonds being made of "plastic alloy," said to be a perfect contact metal.

Michalke, Carl.

Stray currents from electric railways. 101 p. Ill. 1906.

Bibliography, by translator, p. 91-101.

"All the calculations in the text are elementary in character, the rigorous mathematical treatments being given in the footnotes." *Preface.*

Michalke, Carl.

Die vagabundierenden ströme elektrischer bahnen. 85 p. 1906?

Summarizes present (1906) knowledge of destructive electrolysis and presents in an available form much hitherto scattered information from technical periodicals.

Morse, C. H.

Electrolysis of water-pipes. 3,500 w. 1893. (In *Journal of the New England Water Works Association*, v. 7, p. 139.)

Effects and suggested remedies.

Discussion.

Newbaker, C. A.

Cure of electrolysis by independent returns. 4,000 w. Dr. 1900. (In *American electrician*, v. 12, p. 72.)

Prevention of electrolysis; electroless pipe covering on underground piping. 450 w. Ill. 1907. (In *American inventor*, v. 16, September, p. 3.)

Problem of electrolysis. 1,600 w. 1899. (In *Engineering record*, v. 39, p. 465.)

Editorial discussion of the responsibility for damages.

Rasch.

Zur frage der vagabundirenden ströme. 2,700 w. Dr. 1896. (In *Elektrotechnische zeitschrift*, v. 17, p. 34.)

Theoretical, using calculus.

Report of the commission of the German gas and water companies for the investigation of earth currents. 1,500 w. 1906. (In *Electrician*, v. 57, p. 533.)

Outline of report on conditions in nine German cities, 1904-06.

Rhodes, George I.

Some theoretical notes on the reduction of earth currents from electric railway systems by means of negative feeders. 2,500 w. Diag. 1907. (In *Transactions of the American Institute of Electrical Engineers*, v. 26, pt. 1, p. 231.)

Discussion, p. 264. 16,000 w. Diag. dr.

Rowland, Arthur J.

Electrolysis by electric railway return currents. 5,000 w. 1895. (In *Electrical world and engineer*, v. 25, p. 127.)

"Where we have the highest differences of potential [between pipes and rails] the smallest current may be flowing and least electrolytic action taking place."

Rowland, Arthur J.

Electrolysis from electric railway service. 3,800 w. Dr. 1897. (In *American electrician*, v. 9, p. 156.)

Proper road construction to avoid harmful effects.

Sever, George F.

Electrolysis of underground conductors. 25 p. 1904. (In *Transactions of the International Electrical Congress*, St. Louis, v. 3, p. 666.)

Statistical report. Presents five tables giving following data: (1) Street railway practice in U. S. regarding use of return feeders; (2) Recommendations to municipalities by city and other engineers; (3) Electrical features of various municipal ordinances; (4) Summary of opinions of municipal officers; (5) Summary of expert opinion concerning electrolysis.

Discussion.

Sheldon, Samuel.

Conditions of electrolytic corrosion in Brooklyn. 1,600 w. 1900. (In *Transactions of the American Institute of Electrical Engineers*, v. 17, p. 335.)

Discussion, 1,300 w.

The same, without discussion. (In *Electrical world and engineer*, v. 35, p. 868.)

The same, without discussion. (In *Street railway journal*, v. 16, p. 514.)

Siebel, F. P.

Electrolysis of iron pipe. The pitting of iron, particularly pipe, its causes and possible preventives. 3,000 w. 4 ill. 1909. (In *Ice and refrigeration*, v. 37, p. 116.)

Chemical and bacteriological examination of water and of pipe exposed therein. Favors wrought-iron pipe, and recommends city ordinances for prevention of stray currents.

Spang, H. W.

Electrolysis; general electrical and lightning protection. 2,500 w. Dr. ill. 1906. (In *American gas light journal*, v. 84, p. 801.)

Spang, H. W.

Unscientific electric engineering; destruction of underground pipes, etc. 2,500 w. 1904. (In American gas light journal, v. 80, p. 85.)

Stearns, F. P.

Electrolysis on the metropolitan water works. 1,600 w. 1905. (In Engineering record, v. 52, p. 120.)

Abstract of chief engineer's report.

Stone, Charles A. & Forbes, H. C.

Electrolysis of water pipes. 10,000 w. Dr. 1894. (In Journal of the New England Water Works Association, v. 9, p. 25.)

Conditions necessary to destructive action and how trouble may be recognized. Considers all known means of prevention, classifying them as complete remedies, partial remedies, and useless schemes.

Discussion.

Storrs, H. A.

Electrolysis. 4,500 w. Dr. 1895. (In Journal of the New England Water Works Association, v. 10, p. 33.)

Considers remedies where electric roads are already in operation; preventive measures where electric roads are to be installed; legal aspects.

Discussion.

Strecker, K.

Ueber die ausbreitung starker elektrischer ströme in der erdoberfläche. 7,000 w. Dr. 1896. (In Elektrotechnische zeitschrift, v. 17, p. 106.)

For purposes of wireless telegraphy.

Swinburne, James.

Electrolysis of gas mains. 3,000 w. Dr. 1902. (In Electrician, London, v. 49, p. 642, 681.)

Causes, effects, and precautions to minimize injurious effects.

Teichmüller, J.

Ueber methoden zur verringerung der gefahren vagabundirender ströme bei elektrischen bahnen, insbesondere die Kapp'sche methode der schienenentlastung. 2,000 w. Dr. 1900. (In Elektrotechnische zeitschrift, v. 21, p. 436.)

Method making rails the neutral wire of three-wire system.

Ueber die elektrolytische zerstörung der rohrleitungen durch vagabundirende ströme. 9,500 w. Dr. 1900. (In Journal für gasbeleuchtung und wasser-versorgung, v. 43, p. 265, 285, 310.)

Ulbricht, R.

Diskussion über die frage der störungen wissenschaftlicher institute durch elektrische bahnen. 40,000 w. Ill. 1895. (In Elektrotechnische zeitschrift, v. 16, p. 417, 443.)

Paper and lengthy discussion, giving theory of stray currents and conditions causing disturbance of physical laboratories. Many diagrams.

Ulbricht, R.

Gefährdung von metallrohrleitungen durch elektrische bahnen. 2,000 w. Ill. 1902. (In Elektrotechnische zeitschrift, v. 23, p. 720.)

328 CORROSION AND PRESERVATION OF IRON AND STEEL

Ulbricht, R.

Zur frage der gefährdung von metallrohrleitungen durch elektrische bahnen, 3,000 w. Dr. 1902. (In Elektrotechnische zeitschrift, v. 23, p. 212.)

Mathematical treatment of the damage done by stray currents.

Vail, J. H.

Importance of complete metallic circuit electric railways. 5,600 w. Ill. 1894. (In Proceedings of the National Electric Light Association, v. 17, p. 102.)

Advocates proper track bonding, etc.

Discussion.

The same, without discussion. 3,100 w. (In Street railway journal, v. 10, p. 199.)

Vorschlag der erdstrom-kommission des Verbandes Deutscher Elektrotechniker für leitsätze betreffend den schutz metallischer rohrleitungen gegen erdstrome, elektrischer bahnen, 1,500 w. 1903. (In Elektrotechnische zeitschrift, v. 24, p. 376.)

Weber.

Ueber die einwirkung der bodenbeschaffenheit auf gusseiserne röhren. 2,600 w. 1893. (In Journal für gasbeleuchtung und wasserversorgung, v. 36, p. 552.)

West, Jul. H.

Bericht der kommission für die untersuchung der erdrückströme elektrischer bahnen. 1,900 w. 1900. (In Elektrotechnische zeitschrift, v. 21, p. 706.)

Of 90 German cities having electric roads only two or three report corrosion which can be ascribed to earth return currents.

Wynkoop, Hubert S.

Destructive effects of vagrant electricity. 2,000 w. Ill. 1900. (In Popular science monthly, v. 56, p. 357.)

Non-technical article showing destructive effects and suggesting remedies.

Ziehl, Emil.

Verminderung der erdstrome bei mit wechselstrom betriebenen ueberlandbahnen mit schienenrückleitung. 2,800 w. Dr. 1902. (In Elektrotechnische zeitschrift, v. 23, p. 145.)

CORROSION BY SALT WATER

Andrews, Thomas.

Corrosion of metals during long exposure in sea-water. 7,500 w. Ill. 1885. (In Minutes of proceedings of the Institution of Civil Engineers, v. 82, p. 281.)

Andrews, Thomas.

On galvanic action between wrought-iron, cast metals and various steels during long exposure in sea-water. 5,000 w. Ill. 1884. (In Minutes of proceedings of the Institution of Civil Engineers, v. 77, p. 323.)

Anti-fouling compounds. 2,500 w. 1904. (In Scientific American supplement, v. 58, p. 23956.)

Translated from "Farber-zeitung." Deals with preparations for submarine use.

Bell, Benjamin.

On zinc sheathing for ships. 3,400 w. 1869. (In Transactions of the Institution of Naval Architects, v. 10, p. 174.)

Discussion.

Cohen, Ernst.

On the corrosion of condenser tubes and sea-water conductors. 12 p. Pl. 1902. (In Transactions of the Institution of Naval Architects, v. 44, p. 215.)

Describes action of sea-water on brass, copper, and tin-plated condenser tubes.

Coles, Cowper P.

On the preservation of iron ships' bottoms and the means of keeping them clean. 3,400 w. 1866. (In Transactions of the Institution of Naval Architects, v. 7, p. 155.)

Proposes coating the ships' bottoms with cement to prevent corrosion.

Davy, Humphrey.

On the corrosion of copper sheeting by sea-water and on methods of preventing this effect; and on their application to ships of war and other ships. 2,300 w. 1824. (In Philosophical transactions of the Royal Society of London, v. 114, p. 151.)

Considers corrosion of copper an electrochemical action and prevents it by zinc plates in electrical connection with the copper.

Decay of metallic sheathing under water. 900 w. 1907. (In Engineer, London, v. 103, p. 559.)

Abstract of report of the public analyst, New South Wales, concerning the causes of failure of modern Muntz metal.

See also letter from G. A. Muntz, p. 598.

Diegel, H.

Einiges über die korrosion der metalle im seewasser. 95 p. Folding pl. 1903. (In Verhandlungen des Vereins zur Beförderung des Gewerbflusses, v. 82, p. 91.)

The same, condensed. 4,500 w. (In Zeitschrift des Vereines Deutscher Ingenieure, v. 47, p. 1122.)

The same, abstract. 400 w. (In Journal of the Iron and Steel Institute, v. 65, p. 677.)

Extensive experiments lead author to claim that impure metals do not corrode in salt water faster than pure metals. Foreign elements introduced were phosphorus and nickel.

Diegel, H.

Das verhalten einiger metalle in seewasser. 12,000 w. Ill. 1904. (In Stahl und eisen, v. 24, pt. 1, p. 567, 629.)

Considers alloys of copper, nickel, and iron.

Farquharson, J.

Corrosive effects of steel on iron in salt water. 4,800 w. 1882. (In Transactions of the Institution of Naval Architects, v. 23, p. 143.)

Experiments indicating that contact of iron and steel should be avoided.

Discussion.

Ferguson, W. B.

Two instances of unusual repairs to vessels. 3,300 w. Pl. 1907. (In Transactions of the Society of Naval Architects and Marine Engineers, v. 15, p. 179.)

With discussion.

Discussion deals with the serious corrosion of iron and steel bolts used for fastening sheathing, and the advantages of brass composition bolts. Compares merits of copper, zinc, and galvanized-iron sheathing.

Grantham, John.

On copper sheathing for iron ships, considered at the present stage of our experience. 3,000 w. 1869. (In Transactions of the Institution of Naval Architects, v. 10, p. 174.)

Hay, W. J.

On the protection of iron ships from oxidation and fouling. 7,000 w. 1863. (In Transactions of the Institution of Naval Architects, v. 4, p. 149.)

Describes satisfactory use of author's copper oxide paint.

Isherwood, B. F.

Experiments made by Mr. Uthemann to discover a process for preventing the corrosion of copper and brass by sea-water under the conditions found in the surface-condensers of marine steam-engines. 7,600 w. Dr. 1907. (In Journal of the American Society of Naval Engineers, v. 19, p. 601.)

Johnstone, George.

Notes on the serious deterioration of steel vessels from the effects of corrosion. 7 p. 1901. (In Transactions of the Institution of Engineers and Shipbuilders in Scotland, v. 45, p. 71.)

Discussion, 28 p.

Especially on corrosion of internal parts of vessels and on vessels in the tropics.

King, Frank B.

Notes on the corrosion of a cast steel propeller blade. 1,000 w. 1894. (In Transactions of the American Society of Mechanical Engineers, v. 15, p. 961.)

Lewes, Vivian B.

On the corrosion and protection of iron and steel ships. 7 p. 1887. (In Transactions of the Institution of Naval Architects, v. 28, p. 247.)

Discussion, 13 p.

Considers the best preservative composition a gum dissolved in a volatile solvent, mixed with finely divided zinc.

Lidy.

Note sur l'altération des métaux par l'eau de mer. 2,200 w. Ill. 1897. (In Annales des ponts et chaussées, mémoires, ser. 7, v. 14, 3e trimestre, p. 338.)

The same, condensed. 900 w. (In Engineering news, v. 39, p. 85.)

Describes condition of metals after exposure to the action of sea-water for several hundred years.

Mallet, Robert.

On the corrosion and fouling of iron ships. 60 p. 1872. (In Transactions of the Institution of Naval Architects, v. 13, p. 90.)

Discussion, 10 p.

"Catalogue of British patent inventions," p. 135, 17 p.

Pitting of propeller blades. 900 w. 1908. (In Engineer, London, v. 105, p. 535.)

Editorial discussion.

Pitting of propeller blades. 1,300 w. 1909. (In Engineer, London, v. 107, p. 397.)

Editorial discussion, recommending the use of a harder alloy.

Post, J. W.

Corrosion of steel rails by sea water in tropical countries. 400 w. Dr. 1901. (In Engineering news, v. 46, p. 394.)

Rhoades, Henry E.

Corrosion of propeller shaft, U. S. S. Rhode Island. 1,200 w. Folding pl. 1907. (In Journal of the American Society of Naval Engineers, v. 19, p. 379.)

The same, slightly condensed. 1,000 w. (In Mechanical engineer, v. 20, p. 487.)

Sabin, Alvah Horton.

Experiments on the protection of steel and aluminum exposed to sea water. 8,000 w. 1896. (In Transactions of the American Society of Civil Engineers, v. 36, p. 483.)

Condition of plates with various preservative coatings after six months' immersion in sea-water.

Discussion and correspondence.

Sabin, Alvah Horton.

Experiments on the protection of steel and aluminum exposed to water. 5,000 w. 1899. (In Transactions of the American Society of Civil Engineers, v. 43, p. 444.)

Continuation of above experiments.

Discussion.

The same, condensed. (In Engineering news, v. 40, p. 54.)

Sherman, Edward C.

Experiments on the corrosion of steel in contact with bronze in sea-water. 700 w. Diag. dr. 1909. (In Engineering news, v. 61, p. 292.)

See also editorial, p. 292.

The same. (In Mechanical engineer, v. 23, p. 472.)

Results show little loss of steel when protected by zinc strips.

Steinmetz, Joseph A.

Note on corrosion of aluminum. 500 w. Ill. 1903. (In Transactions of the American Electrochemical Society, v. 3, p. 217.)

Corrosion in free-board plates of nickel-aluminium from a dismantled yacht.

"The writer's view is that . . . [the corrosion] was intensified by the use of steel rivets in contact with aluminum plates, uniting them to bronze plates, the whole immersed in salt water and subject to conditions of severe atmospheric changes and exceeding humidity."

Thomson, William.

Notes on the oxidation and corrosion of iron and steel. 2,400 w. 1894. (In Journal of the Society of Chemical Industry, v. 13, p. 118.)

Experiments on the value of protective coatings and on the action of caustic soda, etc., on iron and steel, with special reference to structures exposed to the spray of salt water.

Uthemann.

La corrosion du cuivre par l'eau de mer; moyens de la prévenir. 2,000 w. 1905. (In Le Génie civil, v. 47, p. 344.)

Uthemann.

Corrosion of copper in sea water. 2,800 w. Ill. 1905. (In Engineer, London, v. 99, p. 442.)

The same. (In Journal of the American Society of Naval Engineers, v. 17, p. 467.)

Experiment has failed to produce any alloy which will replace copper for condenser tubes, etc. The paper describes successful attempts to overcome the chemical action of sea-water by electrolytic action between the copper of tubes and the iron of spirals enclosing them.

Uthemann.

Schutz des kupfers und seiner legierungen gegen die zerstörung durch seewasser. 2,000 w. 1905. (In Zeitschrift des Vereines Deutscher Ingenieure, v. 49, pt. 1, p. 733.)

An attempt to determine the best alloys for marine condenser tubes.

Younger, A. Scott.

Corrosion and failure of propeller shafts. 5,500 w. Folding pl. 1900. (In Transactions of the Institution of Naval Architects, v. 42, p. 263.)

Discussion.

Plans suggested as a remedy:

1. Increased diameter of shaft.
2. (a) Re-introduction of outer bearing.
(b) Minimum weight for propeller.
(c) Increased water ballast.
3. Abolish brass liners and run shaft on white metal with oil or tallow surrounding it.

CORROSION BY VAPORS

[Brass corrosion by sugar vapor.] 400 w. 1888. (In American Society of Mechanical Engineers, v. 9, p. 429.)

Remedy suggested is a coating of paraffin.

Dagron, James G.

Protection from corrosion of iron-work used as covering for railroad tunnels. 700 w. Dr. 1892. (In Transactions of the American Society of Civil Engineers, v. 27, p. 324.)

Discussion.

Method for protection consisted of "hermetically sealing the iron-work from the access of steam and locomotive gases by a flat arch of hollow fire-brick tiles."

Dudley, William L.

Effect of coal gas on the corrosion of wrought iron pipe buried in the earth. 1,100 w. 1908. (In Journal of the American Chemical Society, v. 30, p. 247.)

Experiments in earth saturated with coal gas, indicating that amount of corrosion is determined by the chlorine content in the earth.

Friend, J. Newton.

Action of air and steam on pure iron. 2,000 w. 1909. (In *Engineering*, v, 88, p. 526.)

Paper before Iron and Steel Institute.

Concludes that pure iron heated in steam becomes tarnished, and that the action takes place in two stages: first, the dissociation of the steam, second, the union of the dissociated oxygen with the iron and the liberation of free hydrogen.

Kent, William.

Rapid corrosion of iron in railway bridges. 2,000 w. 1875. (In *Journal of the Franklin Institute*, v. 99, p. 437.)

Considers sulphurous acid one of the most active corrosive agents.

Protecting low overhead structures from gases and blasts of locomotives. 1,600 w. 1904. (In *Engineering news*, v. 52, p. 371.)

Report of a committee, presenting opinions from many sources.

Thörner, Will.

Ueber ursache und verhinderung der starken oxydation des eisernen eisenbahn-oberbaues im tunnel. 15 p. Dr. 1889. (In *Stahl und eisen*, v. 9, p. 821.)

Recommends covering the rails with a tar coating and covering the ground and sides with limestone or milk of lime.

BOILER CORROSION

Aynsley, C. Murray.

On the preservation of boilers. 9,000 w. 1880. (In *Van Nostrand's engineering magazine*, v. 23, p. 395.)

Discussion of protective coatings for boilers, action of feed-waters and their treatment.

Baucke, H.

Beitrag zur metallographie des flusseisens. 1,600 w. Ill. 1899. (In *Baumaterialienkunde*, v. 4, p. 349.)

The same, in French. (In *Baumaterialienkunde*, v. 4, p. 349.)

The same. (In *Stahl und eisen*, v. 20, pt. 1, p. 260.)

The same, condensed translation. 600 w. (In *Journal of the Iron and Steel Institute*, v. 57, p. 427.)

Microscopic examination of badly corroded boiler tubes.

Boiler corrosion [and] Boiler incrustation [and] Boiler compositions. 7 p. 1909. (In *Spons' Workshop receipts for manufacturers and scientific amateurs*, revised ed., v. 1, p. 145.)

Boiler incrustations. 9,500 w. 1896. (In *Workshop receipts*, v. 2, p. 42.)

Cary, Albert A.

Cure for corrosion and scale from boiler waters. 7,200 w. Ill. 1897. (In *Engineering magazine*, v. 12, p. 959.)

First of a series of articles. Treats of pitting, grooving and general corrosion, theories in explanation, means of prevention.

Christie, William Wallace.

Corrosion. 35 p. Ill. 1906. (In his *Boiler-waters*, p. 68.)

Treats rather fully the corrosion of boilers, the action of different feed-waters and the dangers of pitting.

Churchill, W. W.

Preservation of surface condenser tubes in plants using salt or contaminated water circulation. 3,000 w. 1906. (In *Science*, v. 47, p. 405.)

The same. (In *Power*, v. 26, p. 598.)

Paper before the American Association for the Advancement of Science.

Considers the prevention of electrolytic corrosion. Author presents Oliver J. Lodge's views on electrolytic conduction and Faraday's laws of electrolysis as a basis for his views.

Corrosion and incrustation; a source of boiler explosions. 2,400 w. Ill. 1908. (In *Boiler maker*, v. 8, p. 279.)

Corrosion of condenser tubes. 1,000 w. Ill. 1909. (In *Mechanical engineer*, v. 24, p. 504.)

Illustrates the appearance and location of the corrosion, and finds it due to stray currents passing through the condenser.

Cribb, Cecil H. & Arnaud, F. W. F.

On the action of slightly alkaline waters on iron. 5,600 w. Ill. 1905. (In *Analyst*, v. 30, p. 225.)

The same, condensed. (In *Engineering*, v. 81, p. 32.)

Experiments indicate increased corrosion in alkaline solution, though less rapid in boilers than under ordinary conditions.

Ford, John D.

Corrosion of boiler tubes. 5,200 w. Ill. 1904. (In *Journal of the American Society of Naval Engineers*, v. 16, p. 529.)

The same, condensed. 1,000 w. (In *Iron and steel magazine*, v. 10, p. 349.)

Extensive experiments made for the United States navy department at the laboratory of the National Tube Co., McKeesport, to determine relative corrodibility of lap-welded Bessemer steel, lap-welded iron, seamless cold-drawn steel and seamless hot-drawn steel boiler tubes.

Frémont, Ch. & Osmond, F.

Les sillons de corrosion dans les toles de chaudières à vapeur. 4,200 w. Ill. 1905. (In *Revue de métallurgie*, v. 2, p. 775.)

Investigation of cause of lines of corrosion in boiler plates.

Gibbons, W. H.

Physical reasons for rapid corrosion of steel boiler-tubes. 800 w. Ill. 1895. (In *American engineer and railroad journal*, v. 69, p. 157.)

Considers difference in corrodibility of tubes made from the "top" and the "bottom" of an ingot, with its application to the relative corrosion of steel and charcoal iron.

Greth, J. C. William.

Chemical aspect of impurities in steam boilers. 3,600 w. 1909. (In *Industrial world*, v. 43, p. 1572.)

Considers the effect of the different impurities in boiler waters and their corrosive influences.

Greth, J. C. William.

Impurities causing scale and corrosion. 4,200 w. 1909. (In *Boiler maker*, v. 9, p. 115.)

Paper before the American Institute of Chemical Engineers.

Discusses action on boilers of salts and acids, the formation of scale and methods of softening the water.

Grossmann, J.

Corrosive action of magnesian and other waters on steam boilers. 2,000 w. Dr. 1909. (In *Engineer*, London, v. 107, p. 262.)

Experiments tend to show that magnesian waters containing in solution also calcium carbonate are not exceptionally corrosive, and that after softening such waters may be more corrosive than in their natural state.

Hopkins, Albert A. ed.

Incrustation of boilers. 600 w. 1901. (In the *Scientific American cyclopedia of receipts*, ed. 2, p. 266.)

Gives receipts for various preventives and remedies.

Huntly, G. Nevill.

Sulphur as a cause of corrosion in steel. 1,600 w. 1909. (In *Journal of the Society of Chemical Industry*, v. 28, p. 339.)

Considers action resulting from the solution of the sulphur present as sulphide in the boiler metal.

Kirtley, William.

On the corrosion of locomotive boilers and the means of prevention. 8,800 w. Ill. 1863. (In *Proceedings of the Institution of Mechanical Engineers*, v. 17, p. 56.)

Considers corrosion due both to chemical action of water and mechanical action of strain. The trouble may be obviated by removing one of these causes, *i.e.*, by proper boiler design, eliminating springing at joints, etc.

La Coux, H. de.

Eaux corrosives et incrusto-corrosives dans les générateurs de vapeur. 14,500 w. 1899. (In *Le Génie civil*, v. 36, p. 117, 139, 149.)

Substances causing corrosion and means of prevention.

Lodin.

Sur les causes d'altération intérieure des chaudières à vapeur. 600 w. 1880. (In *Comptes rendus des séances de l'Académie des sciences*, v. 91, p. 217.)

Chief cause is oxidation due to oxygen set free during decomposition of water.

M'Namara, R. E.

Incrustation and corrosion; causes and prevention in steam boilers and pressure vessels of the varied industries. 2,600 w. Dr. ill. 1909. (In *Boiler maker*, v. 9, p. 63.)

Considers the corrosive ingredients common in boiler waters.

M'Namara, R. E.

Incrustation and corrosion; causes and prevention in steam boilers and pressure vessels of the varied industries. 3,300 w. Ill. 1909. (In *Boiler maker*, v. 9, p. 85.)

Considers especially the attack of corrosive liquids in the packing-house and paper-making industries.

Norris, W. J.

Corrosion in steam boilers. 5,000 w. 1882. (In *Transactions of the Institution of Naval Architects*, v. 23, p. 151.)

Disagrees with theories of galvanic action; production of hydrochloric acid in boiler by decomposition of water; action of fatty acids produced by decomposition of lubricants, etc. Ascribes all boiler corrosion to simple oxidation by presence in water of free oxygen derived from the air.

Palmer, J. Edward.

Corrosion of steel boiler tubes on vessels fitted with turbine engines. 1,000 w. 1907. (In *Journal of the American Society of Naval Engineers*, v. 19, p. 54.)

The same. (In *Engineering news*, v. 57, p. 426.)

Corrosion caused by copper deposits in the tubes, carried over by the steam from the bronze turbine blades.

Paul, James Hugh.

Corrosion in steam boilers. 20 p. Ill. 1891. (In *Transactions of the Society of Engineers*, v. 31, p. 147.)

Chemical properties of iron; manufacture of boiler plates; corrosive natural waters; artesian well waters; corrosion in marine boilers; action of zinc.

Discussion.

Phillips, David.

On the comparative endurance of iron and mild steel when exposed to corrosive influences. 25 p. Dr. 1881. (In *Minutes of proceedings of the Institution of Civil Engineers*, v. 65, p. 73.)

Discussion, 40 p.

Considers admiralty tests and tests by the author indicating greater resistance to corrosion of iron.

Rinne, H.

Kesselmaterial und kesselkorrosionen. 5,000 w. Dr. 1904. (In *Stahl und eisen*, v. 24, pt. 1, p. 82.)

Considers the corrosion of boiler tubes of different qualities of iron and the influence of other conditions.

Rowan, F. J.

On boiler incrustation and corrosion. 2,000 w. 1876. (In *Report of the 46th meeting of the British Association for the Advancement of Science*, p. 229.)

Reviews knowledge and experiments to date (1876) on the action and prevention of corrosion.

Scaife (William B.) & Sons Co.

Corrosion. 900 w. Ill. 1907. (In *their Water purification for all purposes*, p. 47.)

Considers corrosive action of different boiler feed-waters.

Sexton, A. Homboldt.

Study of the corrosion of condenser tubes. 4,500 w. Ill. 1905. In *Engineering magazine*, v. 30, p. 211.)

The same. (In *Journal of the American Society of Naval Engineers*, v. 17, p. 1150.)

Causes and prevention. Considers only brass tubes.

Sickles, E. C.

Corrosion of condenser tubes. 3,000 w. Diag. dr. ill. 1908. (In *Power*, v. 28, p. 349.)

Influence on the choice of condenser equipment for electric power plants.

Summerfield, R. D.

Prevention of scale and corrosion in boilers. 2,400 w. 1900. (In *Electrical engineer*, London, v. 32, p. 91.)

Need of water analysis, treatment of acid waters, etc.

Wakeman, W. H.

Grooving, pitting, and corrosion in steam boilers. 1,800 w. 1906. (In *Industrial world*, v. 40, p. 869.)

Treats briefly of water softening, boiler compounds, galvanic action and action of acid in feed-water.

Worthington, Walter F.

Corrosion of boiler tubes in the United States navy. 5,000 w. Pl. 1900. (In *Journal of the American Society of Naval Engineers*, v. 12, p. 589.)

Causes of corrosion are discussed, especially from the action of the different impurities in feed-water.

Yarrow, A. F.

Some experiments having reference to the durability of water-tube boilers. 2,600 w. (In *Transactions of the Institution of Naval Architects*, v. 41, p. 333.)

Discussion.

From experimental results assumes that both from acid corrosion and from the action of steam nickel steel boiler-tubes will be far more durable than those of mild steel.

PIPE CORROSION

Brackett, Dexter.

Water pipes on metropolitan water works. 2,000 w. 1899. (In *Journal of the New England Water Works Association*, v. 13, p. 325.)

Deals briefly with protection of steel pipe from corrosion. Favors ordinary tar coating, carefully applied, for outside, and paraffin or vulcanite for inside of pipes.

Committee report on relative corrosion of wrought iron and steel pipes. 1,600 w. Dr. ill. 1909. (In *Plumbers' trade journal*, v. 14, p. 214.)

The same, slightly condensed. 1,300 w. (In *Heating and ventilating magazine*, v. 6, p. 12.)

Report to American Society of Heating and Ventilating Engineers.

Tests indicate steel pipe of good quality to be as durable as wrought-iron pipe.

[**Corrosion** of iron water pipe.] 900 w. 1897. (In *Journal of the New England Water Works Association*, v. 11, p. 222.)

Discussion, showing that pipe in which water is standing is less liable to corrosion than that through which water is flowing and thus affording a fresh supply of oxygen.

Corrosion of pipe in coal mines. 450 w. Ill. 1906. (In *Iron age*, v. 78, p. 80.)

Results showing superiority of "Spellerized" steel pipes in the sulphur water of coal mines.

[**Corrosion** of water pipe.] 3,000 w. 1884. (In *Transactions of the New England Water Works Association*, 1884, p. 41.)

Deals briefly with various kinds of service pipes, preferring lead, cement-lined, and galvanized in the order named.

Filling of service pipes by sediment or tuberculation. 1,200 w. 1893. (In Journal of the New England Water Works Association, v. 8, p. 105.)

Topical discussion on pipe corrosion, etc., considering enamel pipe inferior to either galvanized or cement lime.

Freund, Martin.

Über eine eigenartige zerstörung von wasserleitungsröhren. 2,800 w. 1904. (In zeitschrift für angewandte chemie, v. 17, pt. 1, p. 45.)

Investigation of a destructively corroded cast-iron water-pipe, giving analyses of original metal and of the corroded portions.

Greth, J. C. William.

Scaling and corroding substances and their elimination from water for boilers. 5,000 w. 1909. (In Industrial world, v. 43, p. 578.)

Howe, Freeland, jr.

Action of water on pipes. 5,000 w. 1908. (In Journal of the New England Water Works Association, v. 22, p. 43.)

Consideration of the nature of water and of iron pipe and of the electrolytic action that takes place.

Howe, Henry M. & Stoughton, Bradley.

Relative corrosion of steel and wrought iron tubing. 20 p. Ill. 1908. (In Proceedings of the American Society for Testing Materials, v. 8, p. 247.) Discussion, 15 p.

The same. (In Industrial world, v. 83, p. 1244.)

Believes that modern steel tubing is equal to wrought-iron tubing and that the prejudice against it is due to practical experience with other tubing.

Hutton, F. R.

Note on the action of a sample of mineral wool used as a non-conductor around steam-pipes. 2,800 w. 1882. (In Transactions of the American Society of Mechanical Engineers, v. 3, p. 228.)

States that in presence of moisture mineral wool causes very rapid corrosion of iron pipes.

Jamieson, Matthew Buchan.

Internal corrosion of cast-iron pipes. 14 p. Dr. 1881. (In Minutes of proceedings of the Institution of Civil Engineers, v. 65, p. 323.)

Consideration of composition of rust, methods of cleaning pipes and the harmful effects of corrosion.

Murdoch, Gilbert.

Life of cast-iron water pipe at St. John, N. B. 5,000 w. 1894. (In Engineering news, v. 31, p. 15.)

Abstract of report giving cause of pipe failure.

Rust in galvanized iron water service pipe. 6,000 w. 1909. (In Metal worker, v. 71, March 27, p. 48; April 3, p. 52; April 10, p. 45; April 17, p. 48; April 24, p. 39.)

Continued discussion, by letter, in reply to questions by editor concerning the presence and prevention of corrosion in water-pipe.

Siebel, E. P.

Pitting of iron, particularly pipe; its causes and possible preventives. 3,000 w. Ill. 1909. (In National engineer, v. 13, p. 192.)

Paper before the Chicago section of the Society of Brewing Technology.

Siebel, E. P. — *continued*.

Regards pitting as due to electrochemical decomposition in the presence of water and dependent upon the homogeneity of the material. Wrought-iron pipe considered more durable than steel pipe.

Spataro, D.

Corrosion of cast-iron pipes. 800 w. 1893. (In *Journal of the Iron and Steel Institute*, v. 44, p. 522.)

Abstract translation from "L'Industria."

Considers the action of air and water jointly on cast-iron pipes and of the ground in which they are placed.

Speller, Frank N.

Wrought pipe-threading and relative durability of steel and iron. 3,000 w. Dr. ill. 1905. (In *Journal of the Canadian Mining Institute*, v. 8, p. 46.)

The same. (In *Iron age*, v. 75, p. 741.)

Review and illustrations of the United States navy department tests on pitting. Experiments by National Tube Co., showing that, in resistance to corrosion, common iron and Bessemer steel are both slightly superior to charcoal iron.

Stewart, A. W.

Corrosion in metal pipes on board ship. 6,200 w. 1903. (In *Transactions of the Institution of Naval Architects*, v. 45, p. 183.)

The same, abstract. (In *Engineer*, London, v. 95, p. 374.)

Discussion.

Considers the action of impurities on the pipes, especially of chlorine and organic impurities.

Thomson, T. N.

Relative corrosion of wrought-iron and soft steel pipes. 2,800 w. Dr. ill. 1908. (In *Heating and ventilating magazine*, v. 5, p. 15.)

The same, slightly condensed. 2,500 w. (In *Iron age*, v. 81, p. 434.)

See also letter by G. Schuhmann, p. 520.

Paper before the American Society of Heating and Ventilating Engineers.

Conclusion from experiments is that "plain steel pipe is more durable than plain wrought-iron pipe when used to convey hot water and subject only to internal corrosion."

Wrought-iron pipe versus steel pipe. 1,300 w. Dr. 1908. (In *Heating and ventilating magazine*, v. 5, p. 8.)

Contains extracts from a pamphlet published by the Beading Iron Co., claiming that wrought iron is the more durable.

- CORROSION OF STRUCTURAL WORK

Marriott, William.

Strengthening and maintaining of early iron bridges. 10 p. 1905. (In *Minutes of proceedings of the Institution of Civil Engineers*, v. 162, p. 213.)

Discussion, 47 p.

Maintains that no iron bridge rusts as rapidly as new steel bridges, probably due to want of homogeneity or to segregation in the steel.

Preservation of structural steel in tall buildings. 600 w. 1903. (In *Engineering record*, v. 47, p. 129.)

Pabst building, New York City. Steel cage building; framework encased in brick and terra-cotta well preserved.

Removal of a steel frame building. 800 w. 1903. (In *Engineering news*, v. 49, p. 113.)

Good condition of steel in Pabst Hotel, New York City, five years after erection.

Snow, J. P.

Corrosion of structural steel as affected by its chemical composition. 500 w. 1906. (In *Proceedings of the American Society for Testing Materials*, v. 6, p. 148.)

Suggests investigation of part played by manganese and phosphorus.

Taylor, H. N.

Earnest boost for tin roofs. 2,000 w. 1908. (In *Waterproofing and fireproofing*, v. 2, November, 1908, p. 7.)

Claims tin has greater weather-resisting qualities than copper, sheet-lead or zinc.

Taylor, H. N.

Tin is a lasting roofing material; instances in which roofs covered a century ago are still protecting buildings from the weather. 1,600 w. Ill. 1908. (In *Waterproofing and fireproofing*, v. 2, December, 1908, p. 7.)

Taylor, H. N.

Tin roofs on chemically fireproofed sheathing boards. 1,500 w. 1909. (In *Metal worker*, v. 71, p. 44.)

Corrosion of tin from under side, believed to have been caused by moisture coming in contact with the chemicals used in fireproofing the wood.

Thomson, John M.

Chemistry of certain metals and their compounds used in building, and the changes produced in them by air, moisture and noxious gases. 13,000 w. 1896. (In *Journal of the Society of Arts*, v. 44, p. 861, 873, 885.)

PROTECTION AGAINST CORROSION GENERAL

Asbestos protected metal. 600 w. 1908. (In *Railway age*, v. 45, p. 449.)

Sheet-steel is protected by layers of asbestos felt embedded in an asphaltic material.

Birkmire, William H.

Finishing iron and steel. 1,000 w. 1897. (In his *Architectural iron and steel*, p. 156.)

Short chapter on bronzing, enameling, electroplating, galvanizing, painting, and lacquering.

Harper, Robert B.

Comparative values of various coatings and coverings for the prevention of soil and electrolytic corrosion of iron pipe. 25,000 w. Diag. Ill. 1909. (In *American gas light Journal*, v. 91, p. 429, 475, 528, 575, 625, 667.)

Paper before the Illinois Gas Association.

Comprehensive consideration of protection afforded by coatings of different types.

Hiscox, Gardner D. ed.

Plating. 17,000 w. 1907. (In his *Henley's twentieth-century book of recipes, formulas, and processes*, p. 565.)

Description of all methods for the various metals, with many receipts.

See also *Electroplating*, p. 286.

Hiscox, Gardner D. *ed.*

Rust preventives. 2,400 w. 1907. (In his *Henley's twentieth-century book of recipes, formulas, and processes*, p. 623.)

Gives many receipts for preparations and coatings.

Hopkins, Albert A. *ed.*

Rust. 4,500 w. 1901. (In his *Scientific American cyclopedia of receipts*, ed. 2, p. 491.)

Gives methods and formulas of rust preventives for various articles of iron.

Polleyn, Friedrich.

Putzmaterialien für eisen zum entfernen von rost. 28 p. 1909. (In his *Putzbaumwolle und andere putzmaterialien*, p. 218.)

Treumann, Julian.

Die mittel zur verhütung des rostes. 6,000 w. 1898. (In *Stahl und eisen*, v. 18, pt. 2, p. 882, 940.)

Deals principally with methods of rust prevention in structural iron and steel work.

Wood, Matthew P.

Rustless coatings, corrosion, and electrolysis of iron and steel. 432 p. III. 1904.

Gives much valuable information on metal preservation. Deals fully with paints and pigments, galvanizing and other metallic coating processes. Contains bibliographic foot-

CEMENT AND CONCRETE

Action of cinder concrete on steel. 300 w. 1897. (In *Engineering news*, v. 37, p. 186.)

Breuillé.

Expériences sur le ciment armé. 4,500 w. Dr. 1902. (In *Annales des ponts et chaussées, mémoires*, ser. 8, v. 3, 1er trimestre, p. 181.)

The same, condensed. 200 w. (In *Transactions of the American Society of Civil Engineers*, v. 51, p. 124.)

The same, condensed. 100 w. (In *Taylor & Thompson's Treatise on concrete, plain and reinforced*, p. 430.)

Argues against the belief that cement does not attack iron. Chemical union takes place between metal and cement, forming silicate of iron, soluble in water, and unless special care is taken in waterproofing the concrete this salt is dissolved and corrosion takes place.

Buel, Albert W.

Protection of metal work in concrete. 1,400 w. 1898. (In *Engineering record*, v. 38, p. 278, 409.)

Letter claiming that perfect protection may be secured without use of paint.

Buel, Albert W. & **Hill**, C. S.

Preservation of iron in concrete. 1,000 w. 1906. (In their *reinforced concrete*, ed. 2, p. 370.)

The same. (In *American Steel & Wire Company's Handbook and catalogue of concrete reinforcement*. 1908. p. 26.)

Cement paste for protecting steel. 250 w. 1908. (In *Mining and scientific press*, v. 97, p. 744.)

Successful coating used by the Pennsylvania railroad, said to be cheap and durable.

Concrete as a preservative of steel from rust. 1,000 w. 1905. (In *Engineering news*, v. 53, p. 316.)

Editorial emphasizing necessity for proper precautions in applying the concrete.

See also letter, p. 316.

Corrosion of iron in concrete. 3,500 w. 1898. (In *Engineering record*, v. 27, p. 253, 272.)

Corrosion of reinforcing metal. 900 w. 1906. (In *Iron age*, v. 78, p. 1667.)

Summary of report of committee of the Structural Association of San Francisco, recommending the exclusion of cinder concrete as a fireproofing or floor material.

Corrosion of reinforcing metal in cinder-concrete floors. 2,200 w. 1906. (In *Engineering news*, v. 56, p. 458.)

Contains report in full of a committee to the Structural Association of San Francisco, recommending that the building laws be so amended as to exclude cinder concrete from use in floor slabs.

See also editorial, p. 461.

Durability of steel in concrete. 900 w. 1902. (In *Engineering record*, v. 46, p. 280.)

Comment on experiments of Breuillé.

Electrolytic corrosion, and iron and steel in concrete. 1,400 w. 1907. (In *Engineering*, v. 84, p. 430.)

Editorial discussion of recent (1907) experiments.

Experiment to indicate whether iron rusts when imbedded in concrete. 150 w. 1904. (In *Report of the Boston Transit Commission*, v. 10, appendix F, p. 80.)

Two-year tests gave excellent results.

Experiment to indicate whether steel imperfectly cleaned is preserved from further rusting by imbedding the same in concrete. 200 w. 1904. (In *Report of the Boston Transit Commission*, v. 10, appendix F 2, p. 81.)

No apparent increase of rust in two years.

Fox, William H.

Corrosion of steel in reinforced cinder concrete. 1,600 w. Dr. 1907. (In *Engineering news*, v. 57, p. 569.)

Records experiments in which reinforced cinder concrete was exposed to steam and to water for about 40 days. Results showed unmistakable signs of corrosion.

Himmelwright, A. L. A.

Corrosion of steel in cinder concrete. 1,200 w. 1907. (In *Iron age*, v. 79, p. 141.)

Believes that cinder concrete should not be condemned and that the corrosion observed in San Francisco took place during construction.

Hinrichsen, F. Willy.

Zur kenntnis des einflusses von koksasche auf den rostangriff von eisen. 1,400 w. 1907. (In *Mitteilungen aus dem Königlichen Materialprüfungsamt*, v. 25, p. 321.)

Found that the sulphur in coke ashes has very little action on iron enclosed in cement and ashes.

Immunity from rusting of reinforcing steel in concrete. 900 w. Ill. 1908. (In *Engineering news*, v. 59, p. 524.)

Results of tests at the Prussian Royal Testing Institution, showing that ordinary tension cracks do not allow corroding influences of the atmosphere to affect the steel.

Keep water away from steel. 2,700 w. 1908. (In *Waterproofing and fire-proofing*, v. 2, October, 1908, p. 15.)

Claims that by capillary action "steel will draw moisture through two feet of cement." Non-scientific article.

Knudson, Adolphus A.

Electrolytic corrosion of iron and steel in concrete. 3,200 w. Diag. dr. ill. 1907. (In *Transactions of the American Institute of Electrical Engineers*, v. 26, pt. 1, p. 231.)

Discussion, p. 264. 16,000 w. Diag. dr.

The same, without discussion. (In *Electrician*, London, v. 59, p. 213.)

"In no sense can concrete be considered an insulator, and . . . it is from all appearances just as good an electrolyte as any of the soils found in the earth."

Langsdorf, A. S.

Electrolysis of reinforced concrete. 1,200 w. Diag. dr. ill. 1909. (In *Journal of the Association of Engineering Societies*, v. 42, p. 69.)

The same. (In *Engineering-contracting*, v. 31, p. 327.)

In general an amplification of earlier experiments of Knudson, confirming his results.

Lidy.

Expériences sur l'altération des ciments armés par l'eau de mer. 3,000 w. 1899. (In *Annales des ponts et chaussées, mémoires*, ser. 7, v. 18, 4e trimestre, p. 229.)

Results of experiments indicate that cement is not impermeable to salt water and that in time the action of the water will be destructive.

Lindeck, St.

Ueber die elektrische leitungs-fähigkeit von cement und beton. 3,500 w. Dr. 1896. (In *Elektrotechnische zeitschrift*, v. 17, p. 180.)

Gives in tabular form results of many tests proving that for insulating purposes asphalt concrete is superior to cement concrete.

Matthews, Ernest R.

Corrosion of steel reinforcement in concrete. 500 w. 1909. (In *Iron and coal trades review*, v. 78, p. 544.)

The same. (In *Mechanical engineer*, v. 23, p. 441.)

Abstract of paper before the Society of Engineers.

Conclusions are that concrete, properly mixed, gives almost perfect protection to steel, with no need for a cement coating.

More evidence as to possible corrosion of steel imbedded in cinder concrete. 1,400 w. 1906. (In *Engineering news*, v. 56, p. 549.)

Letter from A. L. A. Himmelwright arguing in favor of the use of cinder concrete in floor construction. Writer's belief is that the corrosion observed in San Francisco buildings took place during construction.

See also letter, p. 661.

Newberry, Spencer B.

Chemistry of the protection of steel against rust and fire by concrete. 1,700 w. 1902. (In *Scientific American supplement*, v. 54, p. 22335.)

The same. 1,000 w. (In *Engineering news*, v. 47, p. 335.)

Nicholas, U. James.

Tests on the effect of electric current on concrete. 3,200 w. Ill. 1908. (In *Engineering news*, v. 60, p. 710.)

Shows that electrolytic corrosion of reinforcing steel takes place at that anode, and that under certain conditions concrete and cement are in no sense insulators.

Norton, Charles L.

Corrosion of steel frames of building. 1,500 w. 1902. (In *Iron age*, v. 70, November 6, p. 7.)

Report of the Insurance Engineering Experiment Station of the Associated Factory Mutual Fire Insurance Companies, Boston.

Norton, Charles L.

Corrosion of the steel frames of buildings. 1,800 w. Ill. 1902. (In *Technology quarterly*, v. 15, p. 343.)

Tests showing that concrete to be effective in preventing rust must be dense, without voids or cracks, mixed and applied quite fresh to clean metal.

Norton, Charles L.

Protection of steel from corrosion. 1,600 w. 1904. (In *Engineering news*, v. 51, p. 29.)

Laboratory experiments, tending to show that concrete properly applied is an almost perfect preservative.

Norton, Charles L.

Tests to determine the protection afforded to steel by Portland cement concrete. 1,700 w. Ill. 1902. (In *Engineering news*, v. 48, p. 333.)

Indicate that neat Portland cement is a good preventive of corrosion and that corrosion in cinder concrete is due to rust in the cinders and not to the sulphur.

Preservation of iron in concrete. 700 w. 1903. (In *Engineering record*, v. 47, p. 554.)

Observations on condition of iron embedded in concrete since 1890.

Preservation of materials of construction; an informal discussion. 33 p. Ill. 1903. (In *Transactions of the American Society of Civil Engineers*, v. 50, p. 293.)

Chiefly methods of preventing corrosion of iron and steel when embedded in concrete.

Preservation of steel in ferro-concrete. 1,100 w. 1909. (In *Engineering review*, London, v. 20, p. 352.)

Brief discussion of recent views and work, with special consideration of conclusions of E. R. Matthews, in a paper before the Society of Engineers.

Rohland.

Ueber die oxydation des eisens und den eisenbeton. 400 w. 1908. (In *Tonindustrie-zeitung*, v. 32, pt. 2, p. 2049.)

Iron can be absolutely protected by a concrete coating, owing to the fact that iron is not oxidized by alkaline solutions.

Rohland.

Ueber die ursachen des verschwindens des rostes in eisenbeton. 900 w. 1909. (In *Tonindustrie-zeitung*, v. 33, p. 283.)

Sabin, Louis Carlton.

Preservation of iron and steel by mortar and concrete. 1,100 w. 1905. (In his *Cement and concrete*, p. 336.)

Sabin, Louis Carlton — *continued*

Claims that if properly mixed and applied, both stone and cinder concrete not only prevent corrosion, but arrest the formation of rust when already started.

Schaub, J. W.

Some phenomena of the adhesion of steel and concrete. 1,400 w. 1904. (In *Engineering news*, v. 51, p. 561.)

Points out that a chemical union takes place between the iron and the cement and that this union is dissolved in water.

Steel protecting paste. 300 w. 1909. (In *Compressed air*, v. 14, p. 5252.)

Consists of a mixture of Portland cement, red lead, linseed oil, and a dryer. Used as protection against gaseous fumes.

Taylor, Frederick W. & Thompson, S. E.

Fire and rust protection. 1,400 w. 1905. (In their *Treatise on concrete, plain and reinforced*, p. 427.)

Considers briefly the evidence favorable to protection of both clean and rusty steel by concrete; chemical union of steel and cement, cement paint, etc.

Tests on rusting of steel rods embedded in concrete. 600 w. 1908. (In *Engineering news*, v. 59, p. 525.)

Tests made by J. M. Braxton, United States engineer.

Thwaite, Benjamin Howard.

Preservation of iron and steel. 1,900 w. 1906. (In *Iron and steel magazine*, v. 11, p. 411.)

From "Concrete and constructional engineering."

Calls attention to excellent results obtained by use of cement and concrete coverings.

Toch, Maximilian.

Electrolytic corrosion of structural steel. 1,300 w. Ill. 1906. (In *Proceedings of the American Society for Testing Materials*, v. 6, p. 150.)

Tests of steel embedded in various mixtures of concrete show that the concrete is no protection unless the steel is otherwise insulated.

Toch, Maximilian.

Electrolytic corrosion of structural steel. 1,800 w. 1906. (In *Transactions of the American Electrochemical Society*, v. 9, p. 77.)

The same, without discussion. 1,000 w. (In *Chemical engineer*, v. 4, p. 125.)

The same, condensed. 1,500 w. (In *Electrochemical and Metallurgical industry*, v. 4, p. 215.)

Denies that concrete is a complete protector against corrosion, and cites experiments showing that in structural steel embedded in concrete rapid corrosion takes place at the anode while the cathode is protected.

Toch, Maximilian.

Permanent protection of iron and steel. 2,300 w. Ill. 1903. (In *Journal of the American Chemical Society*, v. 25, p. 761.)

Considers that metal work, coated with cement paint, then with hydrocarbon insulating paint, will be perfectly protected when embedded in masonry.

Turner Construction Co.

Concrete as preservative of steel. 700 w. 1904. (In *Engineering record*, v. 50, p. 146.)

Turner Construction Co.

Experiments on concrete as a preservative of steel exposed to sea-water.
 400 w. Dr. 1904. (In *Engineering news*, v. 52, p. 153.)
 Shows concrete to be an excellent protection against corrosion.

Verhalten von eisen im beton. 400 w. 1903. (In *Stahl und eisen*, v. 23, pt. 1, p. 650.)

Abstract from "Zentralblatt der bauverwaltung."

Only clean iron, free from rust, should be used in concrete, and the rods should not be too near the surface.

Wagoner, Luther, & Skinner, T. H.

Corrosion of reinforcing metal in cinder concrete floors. 2,000 w. 1906.
 (In *Engineering news*, v. 56, p. 458.)

The same. 1,000 w. (In *Engineering record*, v. 54, p. 552.)

Examination of San Francisco buildings after the fire, showing corrosion so great as to render floors unsafe in from six to ten years after construction. Considers presence of coal or coke in cinder especially detrimental and in general condemns the use of cinder concrete.

Whiskeman, James P.

Official report of preservation of structural steel in a tall New York building. 1,800 w. Ill. 1903. (In *Engineering record*, v. 47, p. 394.)

Report to the superintendent of buildings on the Pabst building. Shows that paint is unsatisfactory for underground protection and calls attention to the efficiency of cinder concrete.

ENAMELS AND LACQUERS

Brannt, William T. & Wahl, W. H. ed.

Enamels and enameling. 2,500 w. 1886. (In their *Techno-chemical receipt-book*, p. 115.)

Mainly receipts, with very brief directions.

Cooley, Arnold J.

Enamel. 1,800 w. 1891. (In his *Cyclopedia of practical receipts*, ed. 6, p. 631.)

Receipts mainly.

Enameling. 20,000 w. Dr. 1901. (In *Engineer*, London, v. 92, p. 194, 238, 264, 323, 347.)

Detailed general treatment of the whole subject of enameling.

Grünwald, Julius.

Theorie und praxis der blech- und guessemail-industrie; handbuch der modernen emaille-technik, nebst auszug aus der geschichte der kunstemaille und emailmalerei. 144 p. 1908.

On the raw materials and technical processes, with special reference to industrial enameling.

Hiscox, Gardner D. ed.

Enameling. 20 p. 1907. (In his *Henley's twentieth-century book of recipes, formulas, and processes*, p. 290.)

Reviews steps of process and apparatus, and gives many receipts for enamels.

See also Glazes, p. 377.

Hiscox, Gardner D. ed.

Lacquers. 3,200 w. 1907. (In his *Henley's twentieth-century book of recipes, formulas, and processes*, p. 437.)

Receipts for lacquers for metals and alloys.

Hopkins, Albert A. ed.

Enamels. 4,800 w. 1901. (In his *Scientific American cyclopedia of receipts*, ed. 2, p. 197.)

Hopkins, Albert A. ed.

Lacquering. 5,400 w. 1901. (In his *Scientific American cyclopedia of receipts*, p. 296.)

Receipts for lacquers for the various metals, etc.

Lacquers and paints for metals. 5,000 w. 1903. (In *Engineer*, London, v. 96, p. 264, 288.)

Discusses ornamental rather than purely protective coverings, giving proper methods of application.

Randau, Paul.

Enamels and enameling; an introduction to the preparation and application of all kinds of enamels for technical and artistic purposes; tr. from the German by Charles Salter. 188 p. Ill. 1900.

Rietkötter, Karl.

Die herstellung geschweisster emaillerten behälter. 1,500 w. 8 dr. 1909. (In *Stahl und eisen*, v. 29, pt. 2, p. 1273.)

Schlemmer, J.

Zur entwicklung der emaillierung auf gusseisen und ähnlicher verfahren. 2,000 w. 1906. (In *Stahl und eisen*, v. 26, pt. 1, p. 350.)

Discusses various methods of forming protective coatings on cast iron, whether by ordinary enameling or otherwise.

Standage, H. C.

Practical polish and varnish maker. 260 p. 1892.

Contains many receipts and formulas for varnishes, lacquers and japans for metals.

Underhill, Dillon.

Enameled cast-iron sanitary ware. 7,000 w. Ill. 1909. (In *Foundry*, v. 34, p. 1, 66, 125.)

Series of articles on the manufacture of porcelain enameled ware, in which the methods of moulding, pattern-making, designing, annealing, and enameling are fully discussed.

Vollkommer, Joseph.

Enameling as an industry. 2,600 w. 1899. (In *Iron age*, v. 63, March 23, p. 10.)

Treats especially the preparation of the metal for enameling and the application of the enamel.

Wood, Matthew P.

Rustless coatings for iron and steel; tinning and enameling metals, lacquering, and other preservative methods. 75 p. Ill. 1894. (In *Transactions of the American Society of Mechanical Engineers*, v. 15, p. 998.)

GALVANIZING AND TINNING

Burgess, Charles F.

Investigation of the properties of zinc coatings. 7,000 w. Diag. dr. 1905. (In *Electrochemical and metallurgical industry*, v. 3, p. 17.)

Electrolytic zinc coatings better than metal in the molten condition.

Cold galvanizing; the process and apparatus employed by the U. S. Electro Galvanizing Company. 2,000 w. Dr. 1906. (In *Iron age*, v. 77, p. 1980.)

Collins, A. Frederick.

Cold galvanizing for iron and steel. 1,000 w. 1907. (In *Scientific American*, v. 110, p. 94.)

Considers its advantages over the hot process.

Cowper-Coles, Sherard.

Electro-positive coating for the protection of iron and steel from corrosion. 3,500 w. Ill. 1906. (In *Electrical engineer*, London, v. 44, p. 296.)

Paper before the British Association for the Advancement of Science.

Fully illustrated description of electro-zincing plant and process.

Cowper-Coles, Sherard.

Galvanising of iron and steel surfaces. 4,600 w. Dr. ill. 1905. (In *Iron and coal trades review*, v. 71, p. 1607.)

Paper before the Society of Engineers.

Cowper-Coles, Sherard.

Metallic preservation of iron and steel surfaces. 8,300 w. Ill. 1905. (In *Transactions of the Society of Engineers*, v. 45, p. 183.)

Galvanizing, particularly the sherardizing process of the author.

Discussion. Three folding plates.

Cowper-Coles, Sherard.

Protective metallic coatings for iron and steel. 15,000 w. Ill. 1898. (In *Transactions of the Society of Engineers*, v. 38, p. 139.)

The same, without discussion. 13,000 w. (In *Industries and iron*, v. 25, p. 284, 304, 324.)

Effect of various corroding agents on metals; cleaning by pickling and sand blast; protective zinc coatings.

Discussion. Two folding plates.

Cowper-Coles, Sherard.

Recent improvements in electro-galvanising. 1,300 w. Dr. ill. 1898. (In *Cassier's magazine*, v. 13, p. 306.)

Emphasizes the economy of the process and the durability of the zinc coating obtained.

Cowper-Coles electro-zincing process. 600 w. Ill. 1895. (In *Electrical review*, London, v. 36, p. 119.)

Does not describe process but gives good illustrations of plants in operation.

Davies, Herbert E.

Action of water on zinc and galvanized iron. 5,000 w. 1899. (In *Journal of the Society of Chemical Industry*, v. 18, p. 102.)

Shows that all kinds of water attack zinc and that a moderate degree of hardness favors the action.

Electrogalvanising. 500 w. Ill. 1906. (In *Electrician*, v. 57, p. 533.)

Treatment of boiler and condenser tubes.

Electrolytic tinning. 1,000 w. 1909. (In *Electrical magazine*, v. 11, p. 349.)

Tin is deposited from solution at a temperature of between 50 and 60 degrees.

Flanders, W. T.

Galvanizing. 2,800 w. 1896. (In *Iron age*, v. 57, p. 518.)

Directions for operations in hot galvanizing.

Flanders, W. T.

Galvanizing and tinning. 93 p. Ill. 1900.

Contains forty pages on the practice of hot galvanizing.

Galvanisation électrique du fer. 2,500 w. Dr. 1897. (In *Le Génie civil*, v. 31, p. 38.)

Considers methods of electro-galvanizing, especially those of Wagner and of Cowper-Coles.

Harbord, F. W.

Protecting steel from corrosion. 4,200 w. Ill. 1904. (In his *Metalurgy of steel*, p. 529.)

Brief description of galvanizing and tinning processes.

Lees, T. G.

Internal corrosion of wire ropes. 1,800 w. 1897. (In *Colliery guardian*, v. 74, p. 792.)

Abstract of paper before the Chesterfield and Midland Counties Institution of Engineers.

Describes favorable results obtained by the use of galvanized wire ropes.

Moldenke, R.

Galvanizing. 1,600 w. 1906. (In *Foundry*, v. 27, p. 245.)

Brief consideration of operation of the hot galvanizing process.

Mowry, Edward S.

Electro-galvanizing. 600 w. 1906. (In *Iron age*, v. 77, p. 352.)

Letter claiming marked inferiority of electro-galvanizing to hot galvanizing.

Porter galvanizing process. 1,500 w. Dr. 1904. (In *Iron age*, v. 74, August 18, p. 2.)

Description of machine for removing excess metal on galvanized articles.

Recent developments in galvanizing; "sherardizing," the dry galvanizing process of Cowper-Coles. 1,200 w. Ill. 1909. (In *Scientific American supplement*, v. 67, p. 149.)

Recent improvements in galvanising. 2,000 w. Ill. 1895. (In *Engineer*, London, v. 79, p. 494; v. 80, p. 343.)

Brief notice of early galvanizing and well illustrated description of Cowper-Coles process.

Reese, George C.

On an improvement in the art of galvanizing. 1,400 w. Ill. 1897. (In *Journal of the Franklin Institute*, v. 144, p. 312.)

Improvement consists in removing the excess of zinc coating in a centrifugal separator instead of by the wiping method.

Sang, Alfred.

Art of galvanizing. 9,000 w. 1907. (In *Foundry*, v. 30, p. 417, 486.)

The same. (In *Iron age*, v. 79, p. 1552, 1646.)

Sang, Alfred — *continued*

The same. (In Iron and coal trades review, v. 75, p. 1564.)

The same. (In Scientific American supplement, v. 64, p. 21, 42.)

Paper before the American Foundrymen's Association.

Considers theory of galvanizing and methods in use, with particular reference to sherardizing.

Sang, Alfred.

Electro-cementizing, a process for simultaneously annealing, cleaning, and zinc-coating wire. 2,500 w. 1 dr. 1909. (In Iron age, v. 84, pt. 2, p. 1484.) Trans. Am. Elec. Chem. Soc., XVI, p. 257.

The same. (In Brass world and platers' guide, v. 5, p. 442.)

Paper before American Electrochemical Society, October, 1909.

Coating thoroughly alloyed to metal underneath. Oxides other than zinc may also be used.

Sang, Alfred.

Old and new methods of galvanizing. 10,000 w. 1907. (In Proceedings of the Engineers' Society of Western Pennsylvania, v. 23, p. 546.)

Description of hot and cold methods of galvanizing and of sherardizing. Frequent references to original sources.

Sang, Alfred.

Theory and practice of sherardizing. 2,800 w. Ill. 1907. (In Electrochemical and metallurgical industry, v. 5, p. 187.)

Notes on the operation of the process and on its advantages.

Sexton, A. Humboldt.

Rusting and protection of iron and steel. 26 p. Ill. 1902. (In his Outline of the metallurgy of iron and steel, p. 570.)

Corrosion of various forms of iron, and prevention, chiefly by tinning and other metallic coatings.

Sherardizing; a new process for protecting iron and steel from corrosion. 2,200 w. Ill. 1904. (In Iron age, v. 74, October 20, p. 12.)

Furnace process, invented by Sherard-Cowper Coles, for coating iron and steel with metallic zinc.

Sherardizing; a new method of galvanizing. 800 w. 1908. (In Industrial world, v. 82, p. 250.)

Szirmay, Ignaz.

Erprobung der rostsicherheit von verzinkten eisen- und stahldrähten, sowie von stacheldraht aus verzinkten eisen- und stahldrähten. 1,300 w. 1905. (In Zeitschrift für elektrochemie, v. 11, p. 333.)

Comparative tests of corrodibility of galvanized iron and steel wire and of iron and steel articles galvanized by the hot and the electrolytic processes.

White, Henry I.

Electrolytical galvanizing. 1,600 w. 1906. (In Iron age, v. 77, p. 260.)

Describes process, claiming superiority in protection of iron with a thinner, more even coating.

Wood, Matthew P.

Rustless coatings for iron and steel, galvanizing, electro-chemical treat-

Wood, Matthew P. — *continued*

ment, painting and other preservative methods. 80 p. Ill. 1894. (In Transactions of the American Society of Mechanical Engineers, v. 16, p. 350.)

MAGNETIC OXIDE

Barff.

On the formation of the black oxide of iron on iron surfaces for the prevention of corrosion. 7 p. 1877.

Discussion, 8 p.

Paper before the Liverpool Polytechnic Society. Iron is heated to a cherry-red, then kept in contact with dry steam for several hours. A protective coating of black oxide is formed.

Barff.

Treatment of iron to prevent corrosion. 5,000 w. 1879. (In Journal of the Society of Arts, v. 27, p. 390.)

Discussion, 4,000 w.

Describes author's process of coating with black oxide, giving testimonials concerning the process by its users.

The same without testimonials. (In Scientific American supplement, v. 7, p. 2762, 2778.)

Barff.

Zinc white as paint, and the treatment of iron for the prevention of corrosion. 3,200 w. 1877. (In Journal of the Society of Arts, v. 25, p. 254.)

Discussion, 3,200 w.

Barff process for the protection of iron. 650 w. Dr. 1879. (In Engineering, v. 28, p. 441.)

The same. (In Scientific American supplement, v. 9, p. 3393.)

Bower, George.

On the preservation and ornamentation of iron and steel surfaces. 7 p. 1881. (In Journal of the Iron and Steel Institute, v. 18, p. 166.)

Discussion, 10 p.

Bower, George.

Preservation and ornamentation of iron and steel surfaces. 7,300 w. 1883. (In Transactions of the Society of Engineers, v. 23, p. 59.)

Metal protection by a film of magnetic oxide, produced directly by Barff process and indirectly by joint process of the author and his son. Describes separate processes and the combined or Bower-Barff.

Carulla, F. J. R.

Artificial magnetic oxide of iron. 1,500 w. 1909. (In Engineering, v. 88, p. 532.)

Paper before the Iron and Steel Institute.

Description of a magnetic oxide, early discovered by Gregory and recently introduced by Wüffing, valuable as a protection when applied in the form of a paint.

Gesner rust-proof process. 600 w. Ill. 1890. (In Iron age, v. 45, p. 544.)

The same. (In Industries, v. 8, p. 451.)

Furnace process, giving to iron and steel a dark blue rust-proof coating.

Maynard, George W.

Bower-Barff rustless iron process. 4,000 w. Ill. 1883. (In Transactions of the American Society of Mechanical Engineers, v. 4, p. 351.)

Describes furnace process for covering metals with a coating of magnetic oxide of iron.

Percy, John.

On the protection from atmospheric action which is imparted to metals by a coating of certain of their own oxides, respectively. 1,500 w. 1877. (In Journal of the Iron and Steel Institute, v. 11, p. 456.)

The same. (In Engineering, v. 24, p. 304.)

Iron and copper given as examples.

Platt, Charles.

Oxide films on iron wire. 1,000 w. 1892. (In Engineering and mining journal, v. 54, p. 78.)

Wire exposed to action of steam and acid vapor; heated; dipped in oil bath and again heated.

Sang, Alfred.

Inoxidation processes for protection of iron and steel. 2,500 w. 1909. (In electrochemical and metallurgical industry, v. 7, p. 351.)

Review of processes for protecting iron by a magnetic oxide coating, with full references to original sources.

Thwaite, Benjamin Howard.

On the preservation of iron by one of its own oxides. 13 p. Dr. 1883. (In Minutes of proceedings of the Institution of Civil Engineers, v. 74, p. 215.)

The same. (In Scientific American supplement, v. 19, p. 7625.)

Treats especially the Bower-Barff process.

Weigelin, G.

Inoxydation des eisens. 6,000 w. 1908. (In Stahl und eisen, v. 28, p. 957, 1022.)

Considers the manner and conditions of the formation of a magnetic oxide coating as preservative.

Weigelin, G.

Der inoxydationsofen. 1,800 w. 1904. (In Stahl und eisen, v. 24, pt. 2, p. 1443.)

A type of regenerative gas-furnace used in the Bower-Barff process of coating iron with non-corrosive magnetic oxide.

Weightman, William H.

Oxidation of metals and the Bower-Barff process. 3,000 w. Ill. 1885. (In Transactions of the American Society of Mechanical Engineers, v. 6, p. 628.)

Considers the oxidation of iron and steel by nitre to be superior to the Bower-Barff process in economy, in simplicity of application and in results.

PAINT

Andés, Louis Edgar.

Iron corrosion, anti-fouling and anti-corrosive paints. 275 p. Ill. 1900.

Anti-corrosive paints; their qualities and composition. 4,000 w. 1902. (In *Engineering*, v. 73, p. 837.)

Points out lack of an entirely satisfactory vehicle for metal-protecting paint. Considers the nature and function of dryers. Classifies pigments as basic, acid and neutral, of which only the strongly basic are valuable in metal protection.

Asphalt coatings for water pipe. 1,500 w. 1900. (In *Engineering news*, v. 43, p. 331.)

Tests of various asphalt coatings, leading to the conclusion that "mineral rubber" asphalt is without exception the best pipe covering on the market.

Baker, Ira O.

Tests of bridge paint. 1,200 w. 1899. (In *Railroad gazette*, v. 31, p. 166.)

Summary of experiments.

Bishop, A. J.

Principles underlying car and locomotive painting, describing the various processes and reasons for using materials as they are used. 5,000 w. 1903. (In *Proceedings of the Northwest Railway Club*, v. 8, April, p. 5.)

The same, condensed. 2,500 w. (In *Railroad gazette*, v. 35, p. 437.)

Blanch, Joseph G.

Effect of electricity on paint. 1,300 w. 1905. (In *Proceedings of the American Society for Testing Materials*, v. 5, p. 445.)

Claims that a local electrochemical action takes place between metal surfaces and certain kinds of paint, thereby accelerating internal corrosion.

Blount, Bertram.

Best means of preserving iron and steel work in railway construction. 900 w. 1908. (In *Bulletin of the International Railway Congress Association*, v. 22, p. 31.)

Considers bituminous preparations the best preservatives.

Broom, William.

Information on the preservation of iron and steel structures. 11 p.

Pamphlet considering the properties and value of various paints as metal preservatives.

Butts, H. M.

What advancement has been made in paints for the protection of metal parts and particularly steel cars? 3,000 w. 1904. (In *Proceedings of the Central Railway Club*, May, p. 27; September, p. 12.)

Discussion.

Carulla, F. J. R.

New blue-black iron paint as a protective coating. 1,000 w. 1907. (In *Journal of the Iron and Steel Institute*, v. 75, p. 204.)

The same. (In *Mechanical engineer*, v. 20, p. 446.)

Preservative paint is a by-product obtained from spent chloride pickling liquors.

Cheesman, Frank P.

Priming coats for metal surfaces; linseed oil vs. paint. 2,600 w. 1907. (In *Proceedings of the American Society for Testing Materials*, v. 7, p. 479.)

Cheesman, Frank P. — *continued.*

The same, condensed. 2,000 w. (In *Engineering news*, v. 58, p. 135.)
Considers oil coatings much inferior to paint as preservatives.

Cheesman, Frank P.

Proper paints for metals. 500 w. 1904. (In *American gas light journal*, v. 80, p. 91.)

Letter disapproving of use of boiled oil and of painting machine.

Coating cast iron with tin. 1,000 w. 1909. (In *Railway and engineering review*, v. 49, p. 176.)

Abstract of article in the "*Mechanical World*."

Iron is first given a thin coating of copper, then covered with a metallic paint consisting of a carrier and finely divided tin or tin-lead alloy.

Coffignier, Ch.

Peintures sous-marines et peintures ignifuges. 1,200 w. 1909. (In *Revue de metallurgie*, v. 6, p. 734.)

Cushman, Allerton S.

Inhibitive power of certain pigments on the corrosion of iron and steel. 2,000 w. Dr. 1908. (In *Proceedings of the American Society for Testing Materials*, v. 8, p. 605.)

The same. (In *Engineering record*, v. 58, p. 328.)

Tests were made on the action of air and water combined on about 50 pigments.

Custer, E. A. & Smith, F. P.

Paint as a protection for iron. 7,500 w. 1896. (In *Proceedings of the Engineers' Club of Philadelphia*, v. 12, p. 291.)

Gives as essentials of a proper protective coating: adhesion, non-corrosion, toughness, elasticity and resistance to water.

Discussion.

De Wyrall, Cyril.

Preservative coatings for iron and steel. 900 w. 1901. (In *Proceedings of the American Society for testing Materials*, v. 4, p. 445.)

Considers the vehicle, rather than the pigment, the life of the coating.

Dudley, Charles B.

Tests of paint. 22,000 w. 1904. (In *Engineering record*, v. 50, p. 229.)

Considers only paints for metal protection. Admits that the only reliable test is that of actual service, but believes from experiment that a paint to afford thorough protection must be water-resistant in a greater degree than those now available.

Durability of paints. 2,600 w. 1906. (In *Engineering*, v. 81, p. 90.)

Editorial discussion of experiments of Job and of service tests.

Gardner, Henry A.

Excluding and rust-inhibiting properties of paint pigments for the protection of steel and iron. 12 p. 1909. (In *Proceedings of the annual convention of the Master Car and Locomotive Painters' Association*, v. 40, p. 31.)

The same, condensed. 2,500 w. (In *Engineering-contracting*, v. 32, p. 302.)

Gives Cushman's basic classification of pigments as "inhibitors," "indeterminates," and "stimulators." Gives results of extensive tests of pigments under various conditions.

Gerber, E.

Painting of iron structures exposed to the weather. 101 p. 1895. (In Transactions of the American Society of Civil Engineers, v. 33, p. 485.)

With reference to best methods of rust prevention on inland structures. Describes existing conditions, determined by inspection of more than fifty bridges; paints used; their relative durability, and conclusions arrived at.

Discussion and correspondence.

Gill, Augustus H. & Foster, S. A.

Contributions to our knowledge of white lead and of its protecting properties. 800 w. 1904. (In Technology quarterly, v. 17, p. 145.)

Record of experiments.

Gill, Augustus H. & Johnson, C. C.

Comparison of various tests applied to paints used for the protection of iron. 1,200 w. 1903. (In Technology quarterly, v. 16, p. 32.)

Goodall, Frank C.

Steatite as a pigment for anti-corrosive paint. 2,500 w. 1890. (In Transactions of the Institution of Naval Architects, v. 31, p. 134.)

Discussion, 5,500 w.

Harrison, Arthur B.

Protective coatings for iron and steel. 2,700 w. 1906. (In Engineering record, v. 54, p. 9.)

Classifies protective coatings as: (1) linseed oil paints; (2) varnish and enamel paints; (3) carbon coatings that dry by evaporation. Favors a coating of a certain mineral wax resembling ozokerite, covered by a specially prepared linseed-oil paint.

Hazelhurst, J. N.

Painting. 25 p. 1901. (In his Towers and tanks for waterworks, p. 172.)

Considers chemical and galvanic action upon metals, metal cleaning, and the application of various coatings.

Heckel, George B.

Methods for protecting iron and steel against corrosion. 5,600 w. Ill. 1903. (In Journal of the Franklin Institute, v. 165, p. 449.)

Appendix, 1,000 w.

Reviews recent (1908) work and gives suggestions concerning preservative paints.

Job, Robert.

Protection of structural work from rust. 900 w. 1906. (In American manufacturer and iron world, v. 78, p. 38.)

Claims that the best quality of linseed-oil used with a fine and properly prepared pigment will efficiently protect steel for six years or longer under any ordinary circumstances.

Job, Robert.

Results of an investigation of certain structural paints. 800 w. 1904. (In Proceedings of the American Society for Testing Materials, v. 4, p. 439.)

Discussion, 1,000 w.

Job, Robert.

Results of an investigation of the durability of paints for the protection of structural work. 6,500 w. Ill. 1904. (In Journal of the Franklin Institute, v. 158, p. 1.)

Attributes permanence largely to fineness of pigment.

Koons, Charles.

Protection of iron and steel in car construction, also as applying to building material. 2,000 w. 1902. (In Proceedings of the St. Louis Railway Club, v. 7, July 11, p. 3.)

Attributes successful protection largely to proper cleaning before painting. Various kinds of paint are discussed.

Lawrence, (W. W.) & Co.

Protective coatings for iron and steel. 15 p.

Pamphlet considering the causes of failure in paints and the qualities necessary in a successful coating, with special reference to the products of the Lawrence Co.

Lilly, George W.

Painting and sand-blast cleaning of steel bridges and viaducts. 6,500 w. Dr. 1902. (In Engineering news, v. 47, p. 322.)

Lays stress on thorough cleaning. Calls attention to economy of sand blast and efficiency of pneumatic painting machine. Describes plastering of a viaduct with a composition of Portland cement, red lead, and linseed-oil.

Lilly, George W.

Sand blast cleaning of structural steel. 13,600 w. Ill. 1903. (In Transactions of the American Society of Civil Engineers, v. 50, p. 254.)

Experience in preparing some badly corroded structures for painting.

Discussion.

Lowe, Houston.

Factors that affect results in painting. 3,800 w. 1905. (In Proceedings of the Engineers' Society of Western Pennsylvania, v. 21, p. 197.)

Discussion, 3,200 w.

The same, without discussion. (In Iron trade review, v. 38, p. 44.)

Considers painting of structural work.

Lowe, Houston.

Hints on painting structural steel and notes on prominent paint materials. Ed. 4. 45 p. 1905.

McDonald, Hunter.

Painting railroad bridges. 1,400 w. 1900. (In Railroad gazette, v. 32, p. 265.)

Briefly describes laboratory tests of twenty different kinds of paint.

Mackenzie, William B.

Painting metal bridges. 3,800 w. 1897. (In Canadian engineer, v. 5, p. 67.)

Considers corrosion, oil and pigments. Gives "record of twenty-four painted plates exposed on a steel railroad bridge over an arm of the sea."

Methods of testing the protective power of paints used on metallic structures. 700 w. 1906. (In American machinist, v. 29, p. 794.)

Concludes that durability of anti-rust preparations depends on quality of the linseed-oil used.

One thousand more paint questions answered. 614 p. 1908.

Compiled from the "Painters magazine."

"Painting iron and metal work," p. 102-122. Discusses forty-four separate topics under these heads.

Paint as a preservative of iron from rust. 3,300 w. 1905. (In *Engineer*, London, v. 95, p. 509.)

Chemistry of various paints, giving preference to red lead or red oxide of iron paint.

Paint Manufacturers' Association of the United States — Scientific Section.
Bulletin no. 4, 6-10, 12, 15-16, 19-20.

No. 4. Methods for the analysis of the vehicle constituents of paint. 15 p. .

No. 6. Annual report (1st) of the Scientific section. 93 p. Ill. 1908.

No. 7. Preliminary report on steel test fences. 15 p. Ill. 1908.

No. 8. Report of Committee "E" on preservative coatings for iron and steel. 19 p. 6 pl. 1908.

No. 9. Recent technical developments in paint manufacture. 53 p. Ill. 1909.

No. 10. Protective coatings for conservation of structural materials, by R. S. Perry. 43 p. 1909.

No. 12. The function of oxygen in the corrosion of metals, by W. H. Walker. 16 p. 1908.

No. 15. Protective coatings for structural material, by R. S. Perry. 20 p. 1909.

No. 16. Annual report (1st) on wearing of paints applied to Atlantic City test fence, 1909. 314 p. 23 pl. 1909.

No. 19. Laboratory study of panels of Atlantic City and Pittsburg test fences. 67 p. 32 pl. 1909.

No. 20. Concrete coatings, by H. A. Gardner. 19 p. 1909.

With this is bound a preliminary bulletin, "Physical characteristics of a paint coating," by R. S. Perry. 25 p. 16 pl. 1907.

Paints for iron. 1,200 w. 1899. (In *Engineer*, London, v. 88, p. 29.)

Experiments showing that the most desirable paints are those containing red lead or orange lead.

Paints suited for engineering structures. 4,000 w. 1904. (In *Engineer*, London, v. 97, p. 542; v. 98, p. 41.)

Discusses chemical composition and physical properties of various paints.

Parry, Ernest J. & Coste, J. H.

Chemistry of pigments. 280 p. Ill. 1902.

Describes the uses and methods of application of pigments, the chemistry of the processes of manufacture of the different varieties, methods of analysis, nature of probable impurities, adulterations, etc., and gives analysis of genuine and sophisticated pigments.

Perry, Robert S.

Protective coatings for iron and steel, with discussion. 30 p. 1909.

(In *Paint Manufacturers' Association*, Scientific section. Bulletin no 13.)

Paper before American Chemical Society.

Perry, Robert S.

Protective coatings for structural metal. 19 p. 1909. (In *Journal of the Western Society of Engineers*, v. 14, p. 399.)

With discussion.

Outlines the results of recent investigations and describes a simple accelerated test for durability of protective coatings.

Practicability of establishing standard specifications for preservative coatings for steel. 1,500 w. 1905. (In *Proceedings of the American Society for Testing Materials*, v. 5, p. 426.)

Topical discussion.

Preservation of iron from rust. 4,000 w. 1898. (In *Engineer*, London, v. 85, p. 27.)

Questions the efficacy of linseed-oil and pigments and recommends a "varnish" in which the chief ingredient is pitch or asphalt.

Preservative paints for iron chemically considered. 4,000 w. 1899. (In *Engineering*, v. 67, p. 238.)

Explains the chemical nature and reaction of a single red lead and red oxide of iron paint. Argues strongly against glycerole as an ingredient on account of its hygroscopic nature.

Prevention of rust in iron and steel structures. 1,100 w. 1896. (In *Scientific American*, v. 75, p. 454.)

Editorial plea for greater care in painting, etc.

Protection of iron by paint. 2,600 w. 1897. (In *Engineer*, London, v. 84, p. 389.)

Claims that rusting beneath paint is due not to admission of air through cracks in the paint, but to the hygroscopic nature of the paint, which leads to swelling, porosity and lack of adhesion.

Quest, W. O.

Best method of painting and maintaining steel cars. 2,100 w. 1903. (In *Railway age*, v. 36, p. 332.)

Suggestions for improved methods and better materials.

Report of committee E on preservative coatings for iron and steel. 2,000 w. 1903. (In *Proceedings of the American Society for Testing Materials*, v. 3, p. 47.)

Tentative report suggesting lines for further investigation.

Report of committee E on preservative coatings for iron and steel. 30 p. 1904. (In *Proceedings of the American Society for Testing Materials*, v. 4, p. 137.)

Discussion, 12 p.

The same, condensed. 800 w. (In *Iron and steel magazine*, v. 8, p. 143.)

Compilation of individual opinions of members of the committee concerning best methods of testing preservative coatings.

Report of committee E on preservative coatings for iron and steel. 2,600 w. 1905. (In *Proceedings of the American Society for Testing Materials*, v. 5, p. 79.)

Discussion, 3,000 w.

Report of sub-committees on standard methods of conducting field and service tests, permeability and permanency of paint films, and preparation of iron and steel surfaces for painting.

Report of committee E on preservative coatings for iron and steel. 6,200 w. 1906. (In *Proceedings of the American Society for Testing Materials*, v. 6, p. 47.)

Discussion, 2,300 w.

Experiments begun with different paints on an exposed part of a new bridge of the Pennsylvania Railroad.

Report of committee E on preservative coatings for iron and steel. 1,500 w. 1907. (In *Proceedings of the American Society for Testing Materials*, v. 7, p. 140.)

Describes carrying out of tests started in 1906, method of inspection of condition of paints, etc.

Report of committee E on preservative coatings for iron and steel. 6,500 w.

Folding pl. 1908. (In Proceedings of the American Society for Testing Materials, v. 8, p. 165.)

Contains as appendixes detailed reports of results of analyses of bridge paints by P. H. Walker and P. C. McIlhiney.

Sabin, Alvah Horton.

Industrial and artistic technology of paint and varnish. 372 p. Ill. 1905.

Treats in non-technical language of paints and varnishes, their history, fabrication and uses. Particularly valuable for chapters on rust prevention, and water-pipe coatings. Contains but little chemistry.

Review, 2,200 w. (In Engineering news, v. 52, p. 338.)

Sabin, Alvah Horton.

Paints and varnishes. 5,500 w. 1900. (In Journal of the Association of Engineering Societies, v. 24, p. 146.)

Considers paints and methods for iron protection.

Sabin, Alvah Horton.

Paints for the protection of iron work. 2,800 w. Ill. 1898. (In Engineering news, v. 39, p. 69.)

Shows importance of thorough cleaning of metal surfaces and of thorough drying of one coat of paint before applying another.

Sabin, Alvah Horton.

Protection of metal work. 1,600 w. 1899. (In Engineering record, v. 39, p. 120.)

Insists on complete cleaning of metal and thorough drying of paint.

Sabin, Alvah Horton.

Technology of paint and varnish. 4,500 w. 1904. (In Cassier's magazine, v. 25, p. 330.)

Sabin, Alvah Horton.

Theory and practice of painting on metal. 65 p. Ill. 1905.

Sabin, Alvah Horton.

Theory and practice of protective coatings for structural metal. 8,000 w. 1900. (In Proceedings of the Engineers' Club of Philadelphia, v. 17, p. 87.)

Experiments on metal plates painted with various preparations and immersed in fresh and salt water.

Selby, O. E.

Painting the Louisville and Jeffersonville bridge. 12,000 w. Dr. 1898. (In Transactions of the American Society of Civil Engineers, v. 39, p. 19.)

Methods, cost, etc.

Lengthy discussion and correspondence.

Simon, Edmund.

Ueber die entstehung des rostes unter der das eisen schützenden oelfarbenbedecke. 2,400 w. 1897. (In Dinglers polytechnisches journal, v. 305, p. 285.)

Claims that paint is hygroscopic and permeable to moisture and gases. Abundance of linseed-oil is desirable.

Smith, Harry.

Protective paints for iron. 4,800 w. 1899. (In Journal of the Society of Chemical Industry, v. 18, p. 1093.)

Tests of a large number of paints, indicating red lead and similar pigments as the best preservatives, followed by zinc white and white lead.

Smith, J. Cruikshank.

On the value of physical tests in the selection and testing of protective coatings for iron and steel. 11 p. 1909. (In Journal of the Iron and Steel Institute, v. 79, p. 81.)

The same, condensed. 2,400 w. (In Iron and coal trades review, v. 78, p. 729.)

The same, condensed. 2,400 w. (In Mechanical engineer, v. 23, p. 646.)

The same, condensed. 1,100 w. (In Ironmonger, v. 127, p. 20.)

Discussion and correspondence, 4,500 w., p. 93.

Discusses tests that should be applied to the paint itself and tests of the uniformity, strength, elasticity, permeability, etc., of the paint film.

Spennrath, I.

Protective coverings for iron. 40 p. Dr. 1895?

Gives results of many tests, chiefly on oil paints.

Standage, H. C.

Painting of iron and steel structures. 7,800 w. 1907. (In Painters magazine, v. 34, p. 28, 70.)

Consideration of mechanical, physical, and chemical properties necessary in successful paints, and their application.

Standage, H. C.

Preservation of iron in building structures. 4,000 w. 1897. (In Builder, v. 73, p. 20.)

Detrimental effects of glycerol in paints.

Stebbins, W. L. & Condron, T. L.

Report upon the condition of the ironwork in the old United States post-office and custom house building in the city of Chicago. 1,200 w. 1897. (In Journal of the Western Society of Engineers, v. 2, p. 420.)

Committee report, calling attention to the durability of structural iron when properly painted before erection.

Stern, L. M.

Rust prevention. 54 p. Ill. 1907.

The same, condensed. 5,000 w. (In Iron age, v. 80, p. 1466.)

The same, condensed. 2,200 w. (In Metal worker, v. 68, December 28, p. 42.)

Considers severe conditions of exposure to which metal may be subjected and the preservative paints most suitable.

Taylor, H. N.

About time to paint tin roofs; advice as to the proper pigments to use and methods of application to prevent corrosion and decay, with hints as to material to avoid. 900 w. 1909. (In Waterproofing and fireproofing, v. 3, March, 1909, p. 16.)

Advocates painting tin on both sides and repainting in spring or fall every four or five years. Condemns graphite paints. Gives specifications.

Tests of various paints on the 155th St. viaduct, New York city. 1,000 w. Dr. 1898. (In *Engineering news*, v. 40, p. 14.)

Includes report by Henry B. Seaman.

Tests of various paints on the 155th St. viaduct, New York City, 1,000 w. 1902. (In *Engineering news*, v. 48, p. 164.)

Paints exposed to sulphurous fumes. Carbon paints most durable. Asphalt and rubber compounds unsatisfactory.

Thompson, Gustave W.

Certain solubility tests on protective coatings. 1,500 w. 1908. (In *Proceedings of the American Society for Testing Materials*, v. 8, p. 601.)

Experimental results indicate in general that the best protective coatings are those which contain the lowest percentage of soluble substance.

Toch, Maximilian.

Insulating paints. 2,500 w. 1905. (In *Transactions of the American Electrochemical Society*, v. 8, p. 133.)

Mainly an outline of necessary qualities and of suggestions for research.

Toch, Maximilian.

Protection of steel against corrosion. 3,500 w. 1908. (In *Transactions of the American Electrochemical Society*, v. 14, p. 207; v. 15, p. 391.)

Discussion, 700 w.

Shows the weakness of mediums "for inhibiting corrosion of iron or steel in transit" and emphasizes the necessity for insulating paint at contact-points of two pieces of steel.

Todd, James.

Protective coatings for structural material. 800 w. 1909. (In *Railroad age gazette*, v. 46, p. 1018.)

Letter on the use and preparation of linseed-oil as a protective coating.

Tolmer, M. L.

Preservation, maintenance and probable durability of rolling stock with metal underframes and metal upperframes. 3,400 w. Dr. 1896. (In *American engineer, car builder, and railroad journal*, v. 70, p. 171.)

Results of careful investigation by Eastern Railroad of France. Recommends cleansing and painting of metal underframes every three years. Metal upperframes do not greatly lengthen the life of the car. Machine riveting has great advantages over hand riveting in rust prevention. Estimates useful life of cars at fifty to sixty years, depending on type. Diagrams show extent of corrosion.

Toltz, Max.

Paint tests. 5,000 w. 1896. (In *Journal of the Association of Engineering Societies*, v. 18, p. 351.)

Classifies paints. Outlines a method of iron and steel painting arrived at after careful consideration.

Discussion.

See also v. 19, p. 175.

Value of white paints on engineering structures. 3,500 w. 1903. (In *Engineer*, London, v. 96, p. 227.)

Explains lack of durability of white paint.

What is the best method of painting steel cars? 2,200 w. 1905. (In *Proceedings of the American Society for Testing Materials*, v. 5, p. 436.)

Considers both new cars and repainting. Lays stress on painting immediately after cleaning.

Whited, Willis.

Bridges. 5,500 w. 1906. (In Proceedings of the Engineers' Society of Western Pennsylvania, v. 22, p. 141.)

The same, condensed. (In Railway and engineering review, v. 46, p. 631.)

Design and painting of bridges.

Discussion.

Wilgus, W. J.

Paint tests. 1,200 w. 1897. (In Journal of the Association of Engineering Societies, v. 19, p. 175.)

Discussion of paper by Max Toltz. Outlines methods for iron painting considering both new work and repainting.

Wood, Matthew P.

Protection of ferric structures. 63 p. 1901. (In Transactions of the American Society of Mechanical Engineers, v. 22, p. 757.)

Discusses both successful and unsuccessful examples.

Wood, Matthew P.

Rustless coatings for iron and steel. 40 p. Ill. 1897. (In Transactions of the American Society of Mechanical Engineers, v. 18, p. 251.)

Wood, Matthew P.

Rustless coatings for iron and steel; paints: of what composed, how destroyed, classification as true pigments and inert substances, adulterants, etc. 43 p. 1895. (In Transactions of the American Society of Mechanical Engineers, v. 16, p. 663.)

Wright, J. D.

Best method of painting and maintaining steel cars. 1,700 w. 1903. (In Railway age, v. 36, p. 331.)

Composition and application of paints.

PAPER

Andés, Louis Edgar.

Anti-corrosive weatherproof paint containing paper. 200 w. 1900. (In his Iron corrosion, anti-fouling and anti-corrosive paints, p. 240.)

The same. (In his Der eisenrost, p. 252.)

Process of Cross & Bevan by which cellulose paper is dissolved in caustic soda lye, etc., producing a highly protective paint.

Barker, Louis H.

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Tabular results of paint tests, with remarks on the value of paraffin paper as a protective covering.

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Describes Barker's successful use of paraffin paper as a protecting material.

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